

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Crude Oil Samples

4.1.1 Water in Crude Samples

The amount of water in the crude oil determined by modified KF method (ASTM D 4928) and toluene method (ASTM D 4007) are shown in Table 4.1 and Figure 4.1. Percent of water in the crude could be determined more accurately by the KF method than toluene method, because water and crude were homogenized in the toluene solution and the crude sample was then pipetted to KF titrator for water analysis. The toluene method determined water separation after homogenized water-crude-toluene was equilibrated for 3 hour and the free water separated was in equilibrium with water in the crude and in emulsion phases. Therefore determination of total water by toluene method is most likely less than the KF method. The toluene method is useful for determination of free water separated and water distribution in other phases as shown in Figure 4.1.

Table 4.1 Amount of water in crude oil from each well by using KF method

Well	%water	% SD
A 07T	71.82	1.38
C 10T	17.92	0.27
D 12T	39.70	0.43
F 09T	2.20	0.40
F 10T	24.36	1.48
W 05T	8.00	0.00

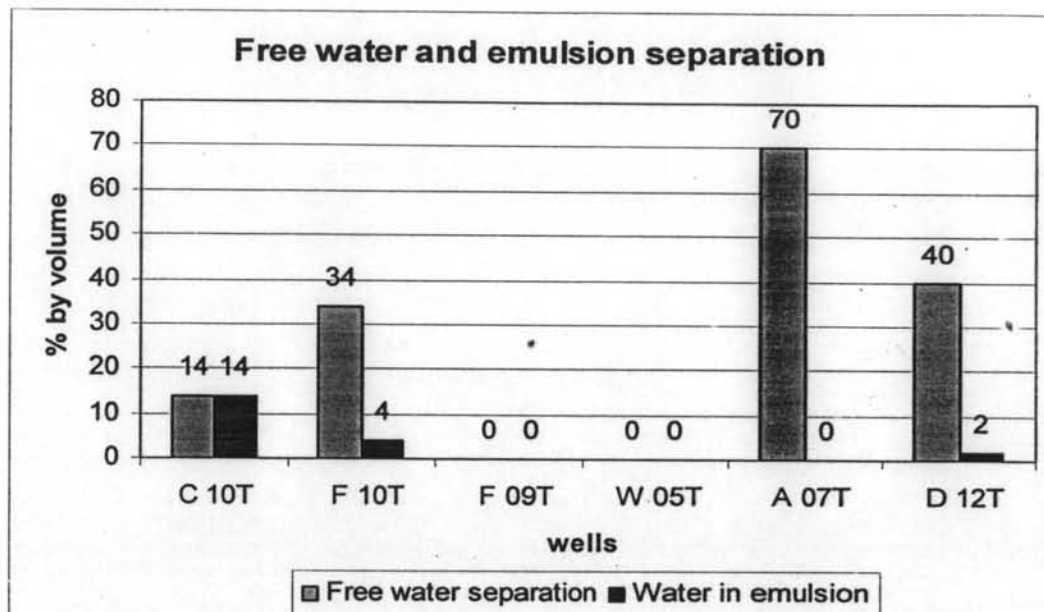


Figure 4.1 Free water and emulsion separated by the toluene separation method (ASTM D4007) at 60 °C.

4.1.2 Viscosity of Crude Oils

The amount of water in crude oil was related to its viscosity of crude oil. The result of viscosity at 56-57 °C is shown in Table 4.2. When the water exerted in the crude oil, the viscosity of the crude oil was significantly increased. In other word, the higher the water content, the higher the viscosity of the crude oil.

Table 4.2 Viscosity of crude oil by Brookfield at 56-57 °C

Well	%Water in crude oil	Viscosity (cP)
A 07T	71.82	284
C 10T	17.92	69.5
D 12T	39.70	157
F 09T	2.20	53.8
F 10T	24.36	58
W 05T	8.00	53.2

4.1.3 Asphaltene and Sediment

The amount of asphaltene and sediment in crude oil from different well were investigated and shown in Table 4.3. The amounts of asphaltenes found in all crude were varied from 1% to 7%. Generally accumulation of asphaltenes at the water oil interface results in the formation of rigid film. An asphaltenes-stabilized water droplet dispersing in oil phase as illustrated in Figure 4.2, the asphaltenes forms a film which acts as a barrier to droplet coalescence. To separate water from crude oil, water-in-oil emulsion must be destabilized and the film has to be drained and ruptured. Normally the asphaltenes content can vary from 3 to 70 % (wt/wt). From our results, it can be said that asphaltenes has less effect on emulsion stability.

Table 4.3 The amount of asphaltenes and sediment presenting in the crude oil

Wells	Asphaltene+other sediments		Asphaltene		Sediment	
	(g)	%	(g)	%	(g)	%
A07T	0.1368	2.74	0.1105	2.21	0.0263	0.53
C10T	0.2597	5.19	0.2338	4.68	0.0259	0.51
D12T	0.129	2.59	0.1169	2.34	0.0127	0.25
F09T	0.4113	8.23	0.3679	7.36	0.0434	0.87
F10T	0.1629	3.26	0.1413	2.83	0.43	0.43
W05T	0.0748	1.50	0.0693	1.39	0.0055	0.11

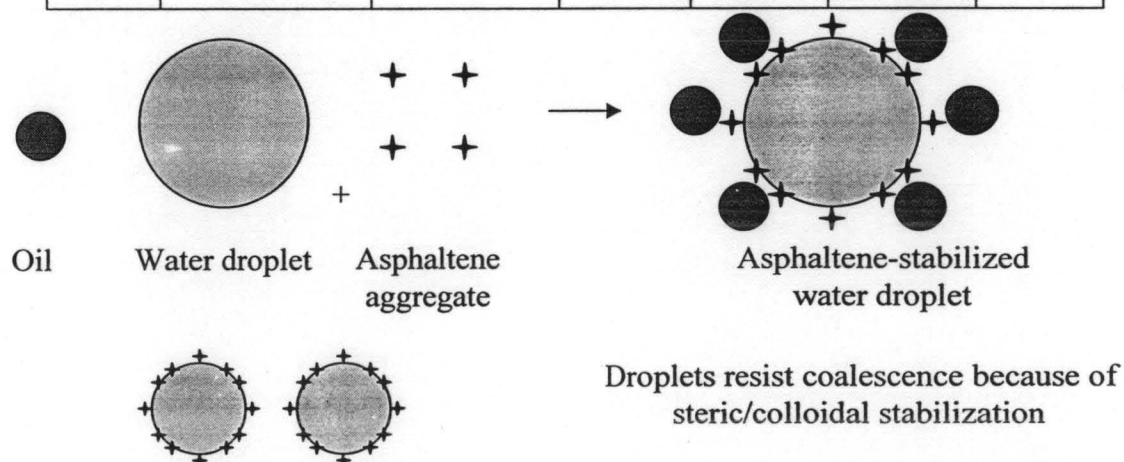


Figure 4.2 Mechanism of emulsion stabilization by asphaltenes (Kokal, 2005).

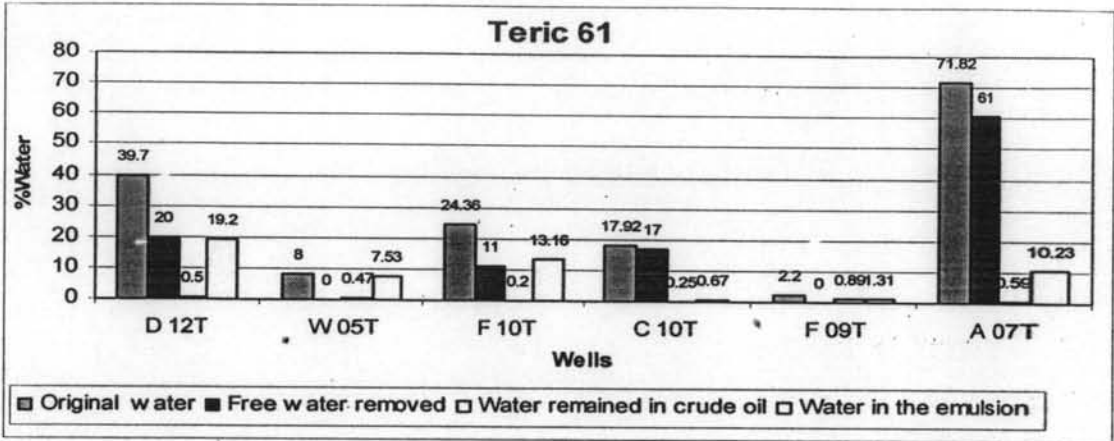
4.2 Screening of the Demulsifiers

The bottle test was used to determine the capability of the investigated demulsifiers in breaking 6 crude samples separate free water. The accuracy level with 0.5 % could be achieved by this method. The amount of demulsifier was 1000 ppm (w/w) at 60 °C. In this study the demulsifiers was divided into 2 main types, non-ionic surfactants (EO/PO block-copolymers and phenolic glycol) and ionic surfactants (sulphosuccinate salt and fatty alcohol polyglycol ether sulfate). After water was separated from the crude sample, water remaining in the crude was determined by KF method and water remaining in the emulsion by mass balance.

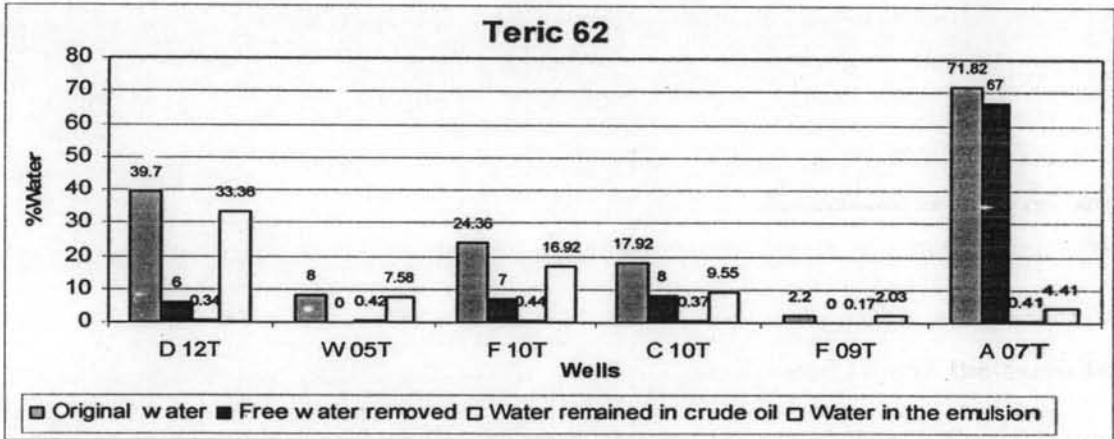
4.2.1 Nonionic Surfactants

4.2.1.1 *EO/PO Block-Copolymer: Teric Series*

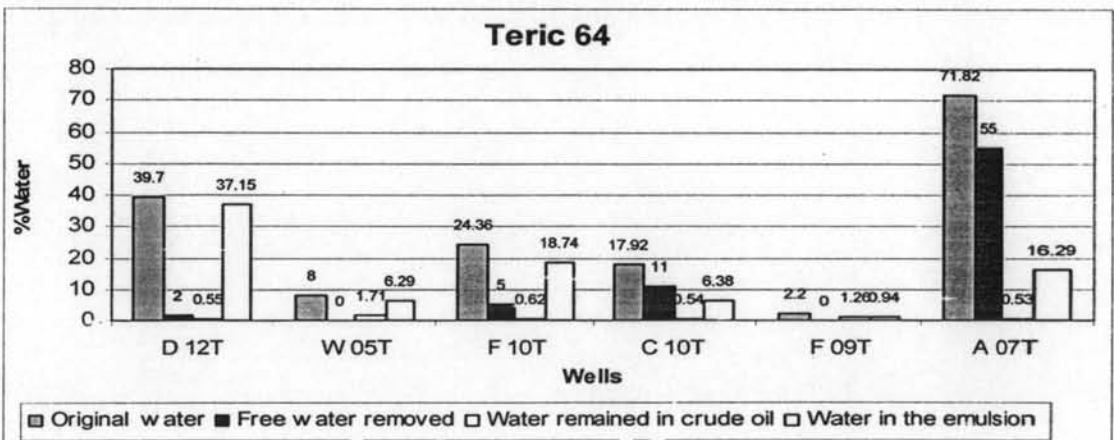
Figures 4.3 (a – e) showed the results of the bottle test for Teric series. There was remnant water in crude oil was mostly less than 0.5 % as required by the oil industry. Teric 61 showed the best efficiency for water separation from most of the crude oil sample, which Teric 87 was the best for crude W 05T which water could not be separated by other Terics. Teric 62 also showed the best water separation from crude A 07T. It would be explained by cloud point of surfactants. The cloud points of Teric 61, Teric62, and Teric 87 are in the range of 16 °C to 18 °C , 22 °C to 24 °C, and >100 °C respectively. For the other Terics, the cloud points were above the operating temperature (60 °C). The cloud point is the temperature below which a single phase of molecule or micellar solution exists; above the cloud point the surfactant loses sufficient water solubility from the structure of the PO and EO of nonionic surfactant. For a particular hydrophobic group, the larger the percentage of ethylene oxide in the surfactant molecule, the higher the cloud point. The phase separation occurs due to dehydration of ethylene oxide in the hydrophilic group when the temperature is increase and the micellar formations alter the interaction of oil and thus release water from oil. The phase separation also occurs due to the difference in density of the micelle-rich and micelle-poor phase.



a



b



c

Figure 4.3 (a-e) Water separation by bottle test using Teric series of demulsifiers at 60°C.

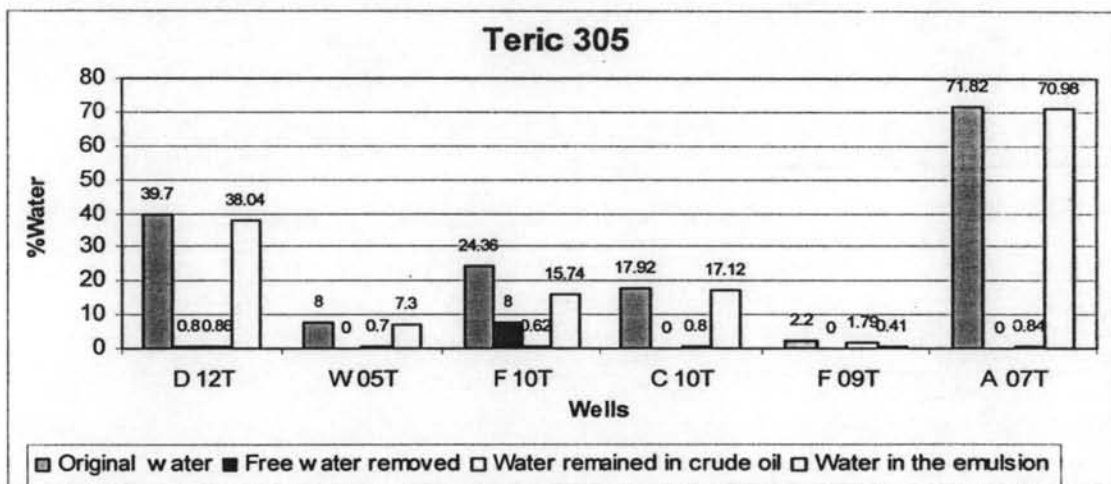
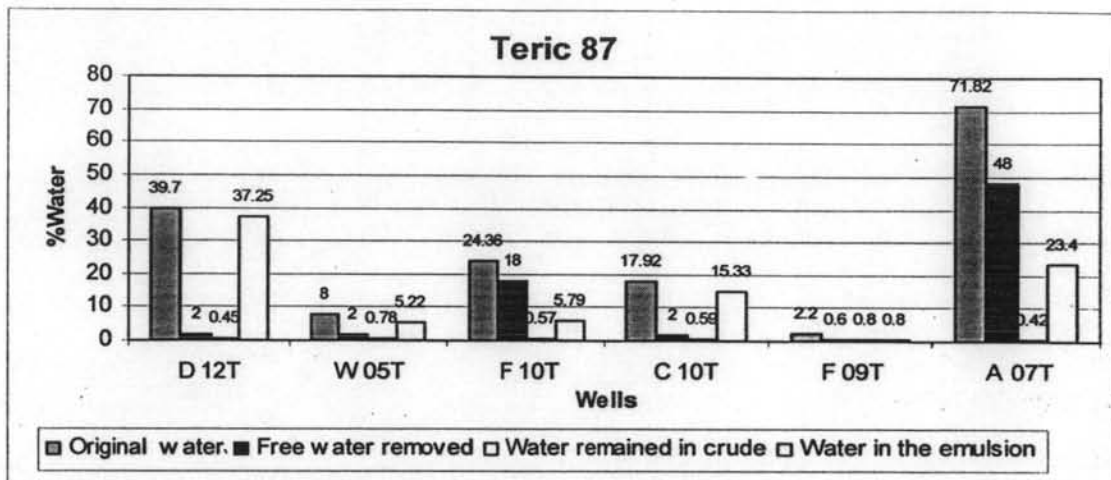


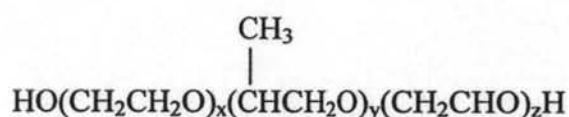
Figure 4.3 (a-e) (cont.) Water separation by bottle test using Teric series of demulsifiers at 60°C.

Phase separation consists of oil, emulsion, and free water phase. When water in crude is separated by the action of demulsifier, the water may become free separated phase as be emulsified and increase volume of emulsion phase. Example can be illustrated by Teric 305, most water separated from crude is emulsified and increase the volume of emulsion phase. Emulsion which is a middle phase between free oil and free water phases still composes of water and crude oil. For the most effective demulsifier, this emulsion phase should be minimized in order

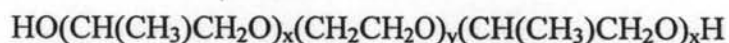
to obtain the most crude oil. Teric 61 showed the most effective demulsifier among the Teric series.

4.2.1.2 EO/PO Block-Copolymer: Pluronic Series

The Pluronic series are block copolymer that the structures were EO-PO-EO or sequential block copolymers and PO-EO-PO or reverse sequential block copolymers. The sequential block copolymers exhibit more hydrophilic than the reverse block copolymers as shown in Figure 4.4. Water separation by Pluronic series are shown in Figures 4.5 (a-i). Pluronic PE6100 and Pluronic RPE3110 worked the best for crude F 10T for the most water separation and water remaining in the crude, the reason were the cloud point. Pluronic PE6100 and Pluronic RPE3110 are 23 °C and 21 °C, respectively. The efficiency of Pluronic series were not only depend



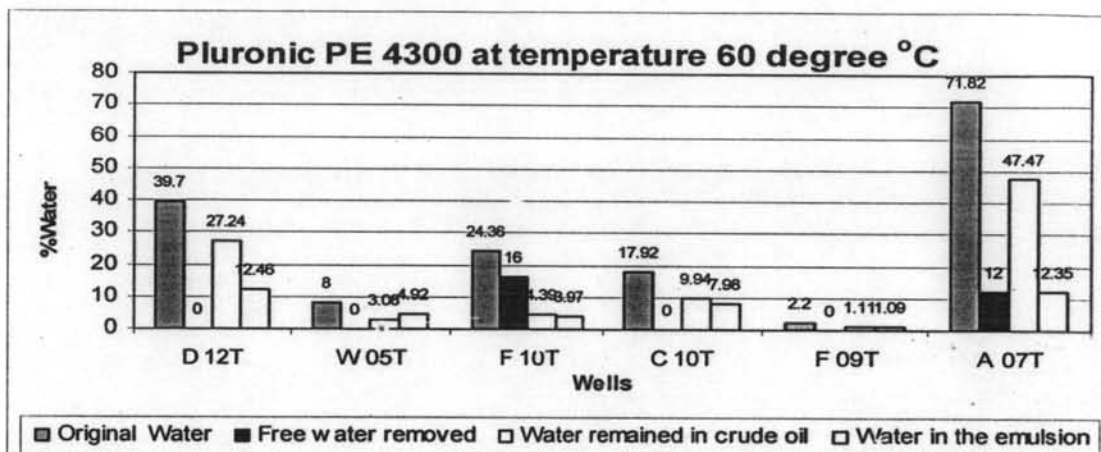
Sequential block copolymer



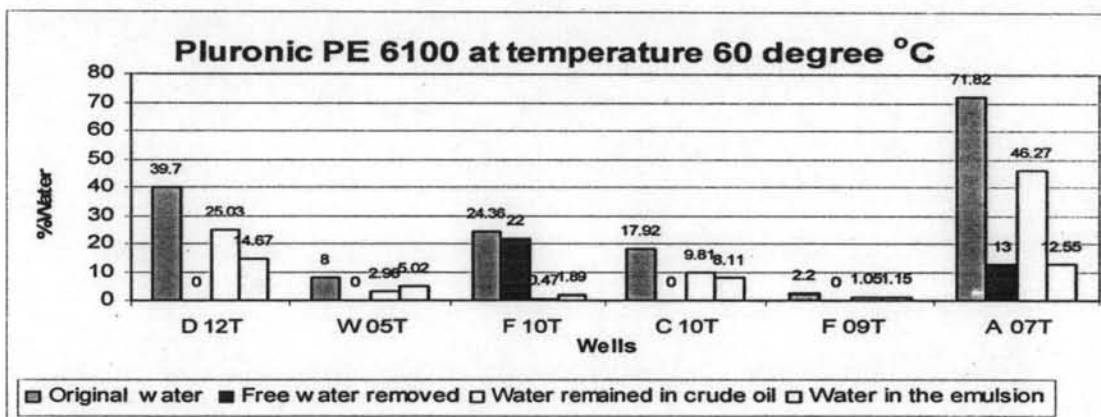
Reverse sequential block copolymer

Figure 4.4 Show the structure of Pluronic PE and Pluronic RPE series.

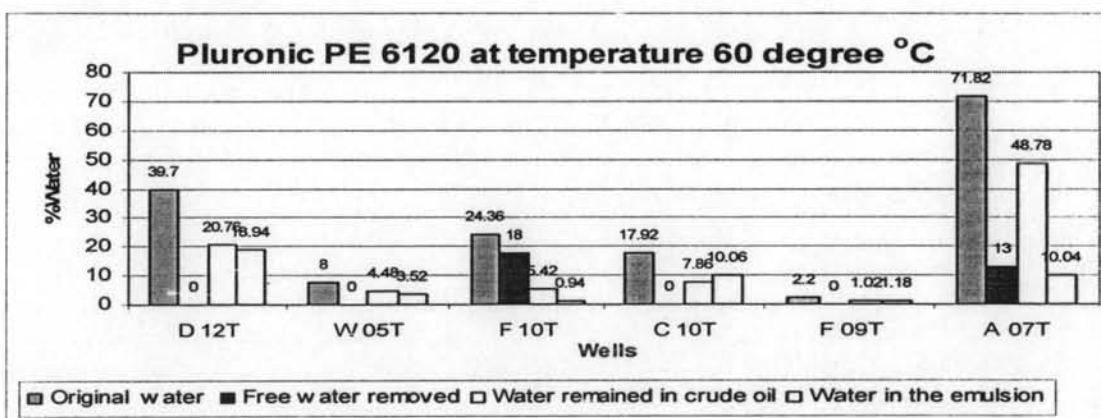
on cloud point but the structure also. The Pluronic PE is block copolymers that the central polypropylene glycol group is flanked by two polyethylene glycol groups while The Pluronic RPE is consist of block copolymer that central polyethylene oxide block is flanked by two polypropylene oxide blocks. Comparison in term of cloud point ranging from 21 °C -23 °C between Pluronic PE6100 (cloud point 23 °C) and Pluronic RPE3110 (cloud point 21 °C), the PE series will gave higher efficiency than RPE series. Generally, the demulsification performance of sequential block copolymer was better than reverse ones (Jiangying *et al.* 2005). In the same manner, the results from Pluronic PE groups were better than Pluronic RPE groups since it can remove free water at least F 10T and A 07T but Pluronic RPE can remove free water only from F 10T.



a



b



c

Figure 4.5 (a-i) Water separation by bottle test using Pluronic series of demulsifiers at 60°

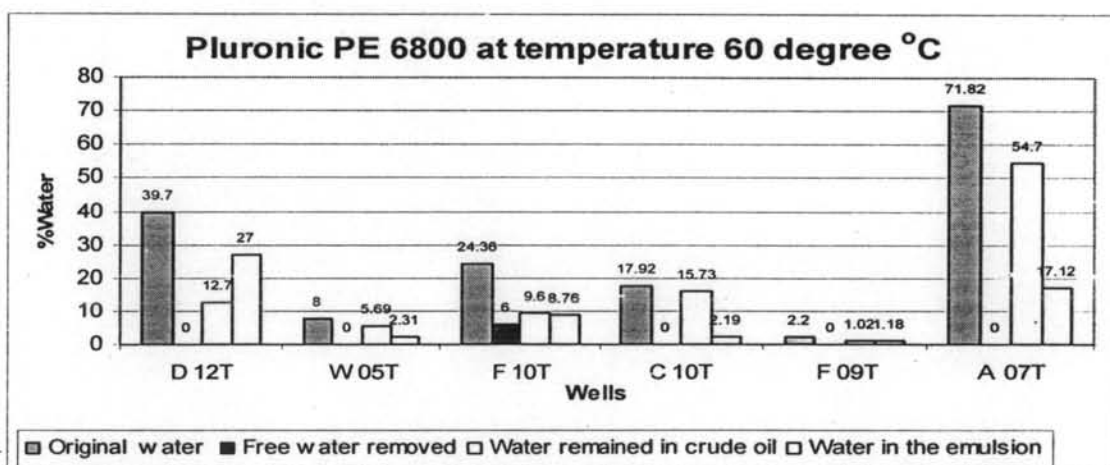
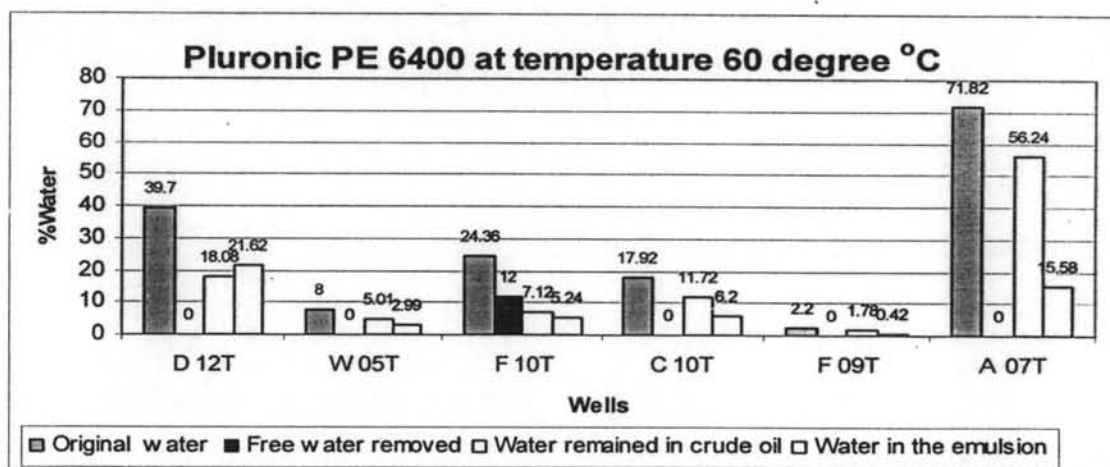
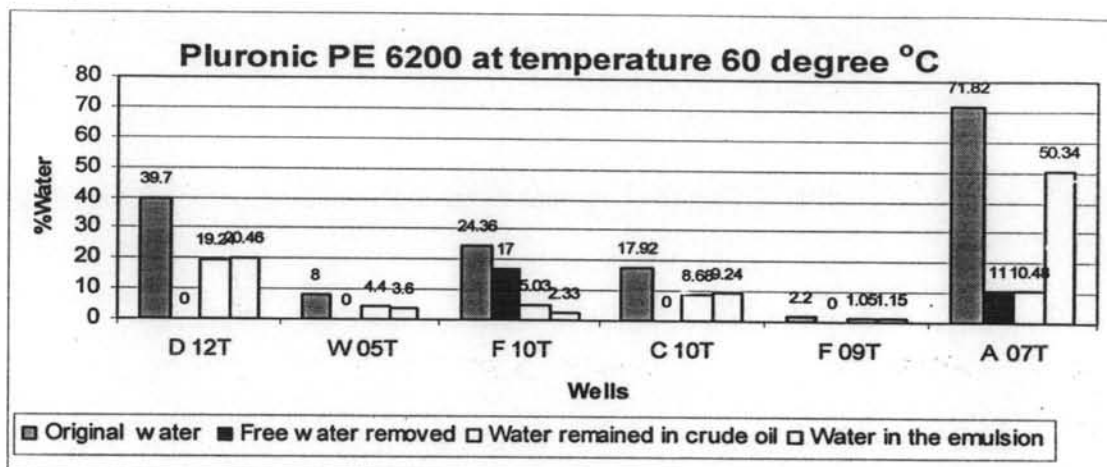
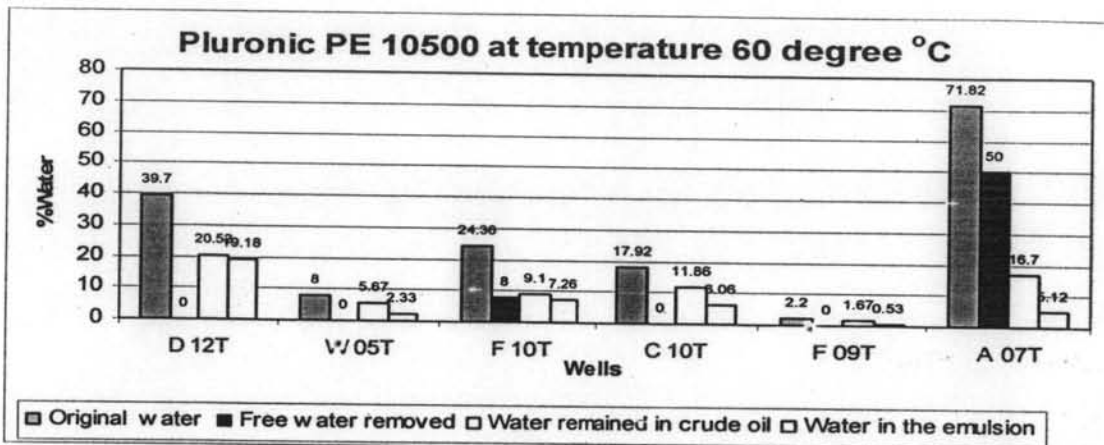
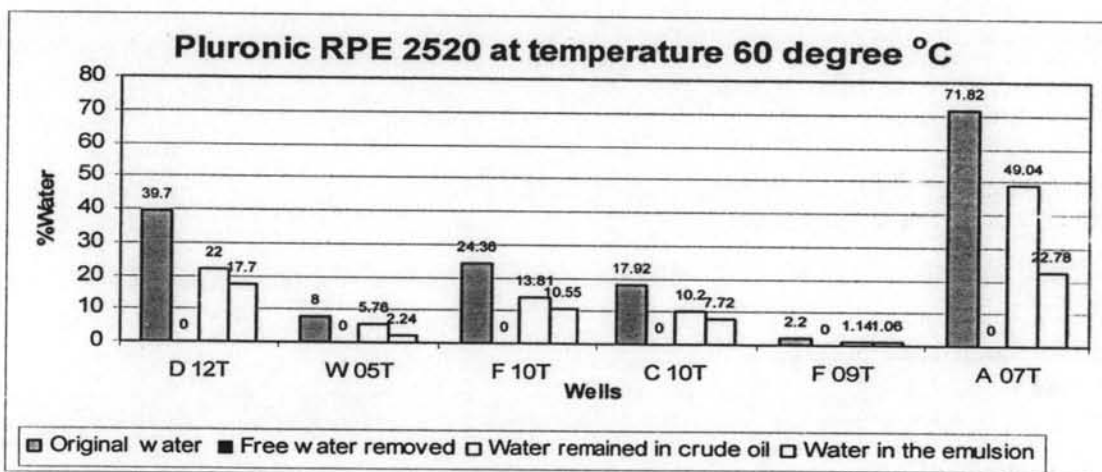


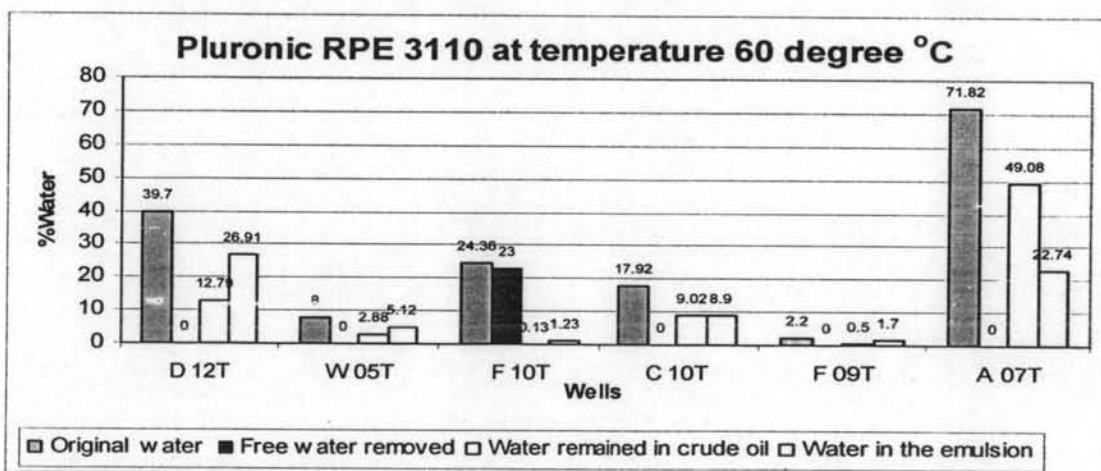
Figure 4.5 (a-i) (cont.) Water separation by bottle test using Pluronic series of demulsifiers at 60°C.



g



h



i

Figure 4.5 (a-i) (cont.) Water separation by bottle test using Pluronic series of demulsifiers at 60°C.

4.2.1.3 Nonyl-Phenol Series

Water separation by demulsifiers, NP series are shown in Figures 4.6 (a-c). Nonyl phenol series gave water separation for two wells (F 10T and A 07T), however the water remaining in the crude was still high. These results again can be explained by the cloud point of the NP series. The NP 6 is insoluble in water phase, so its cloud point should be very low. The separation of free water was as well as Teric 61 for the two crudes.

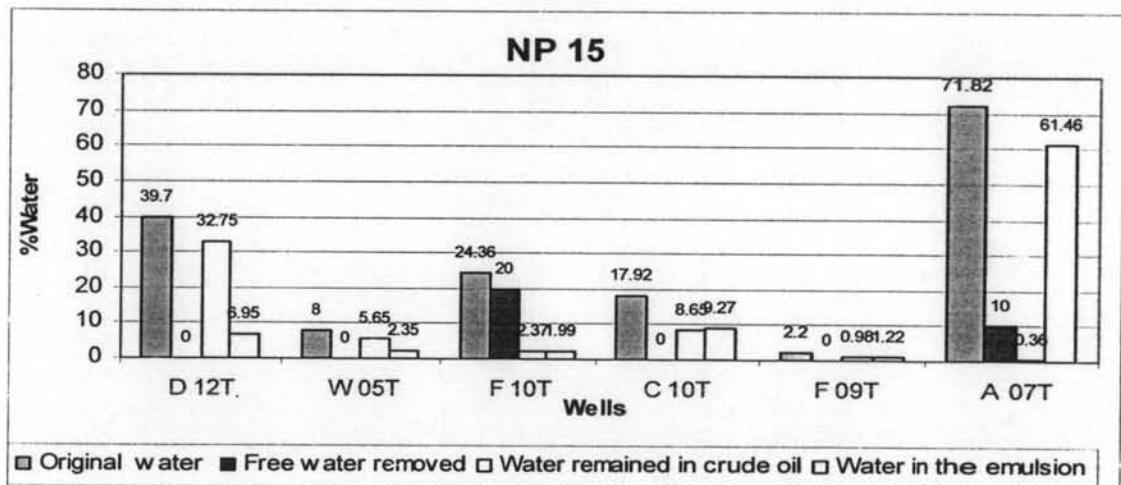
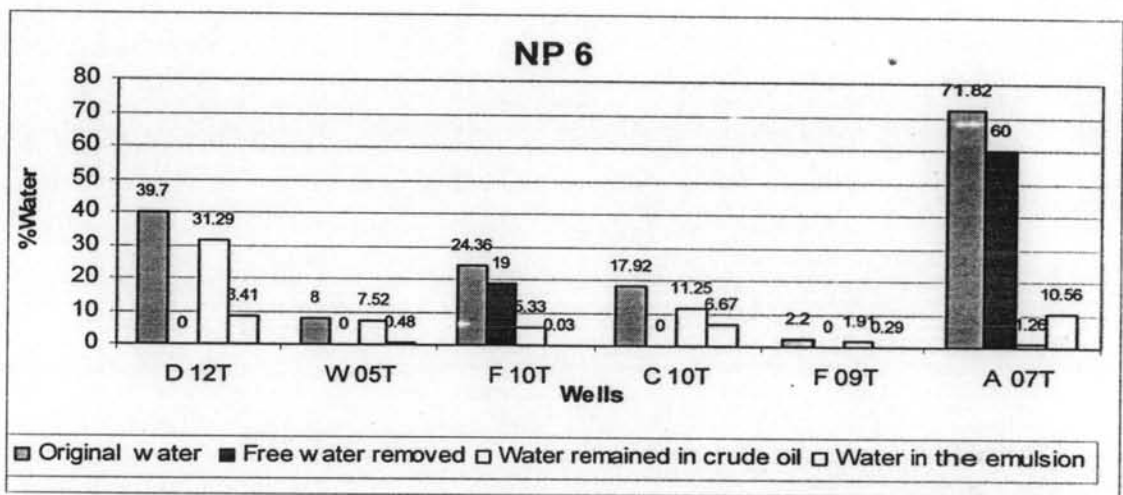
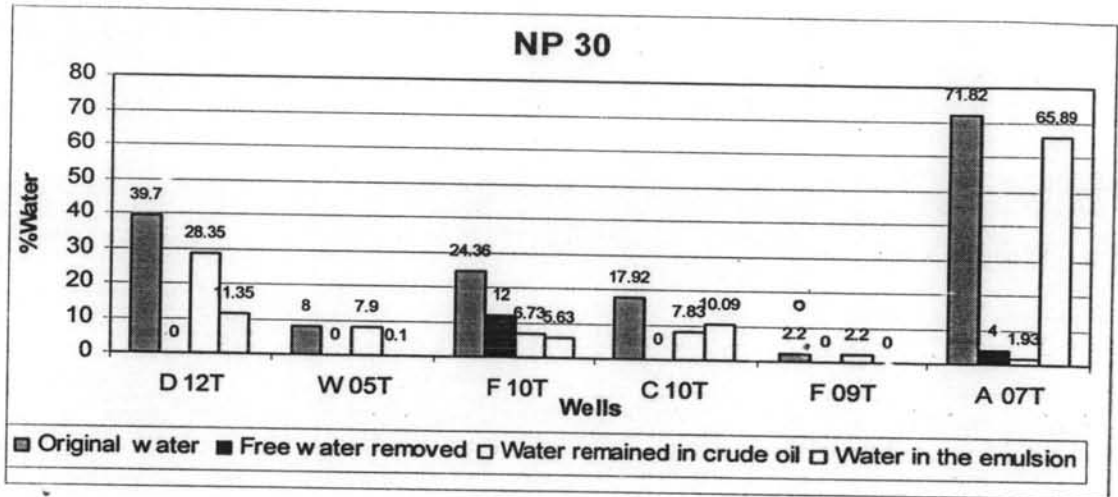


Figure 4.6 (a-c) Water separation by bottle test using NP series of demulsifiers at 60°C.



c

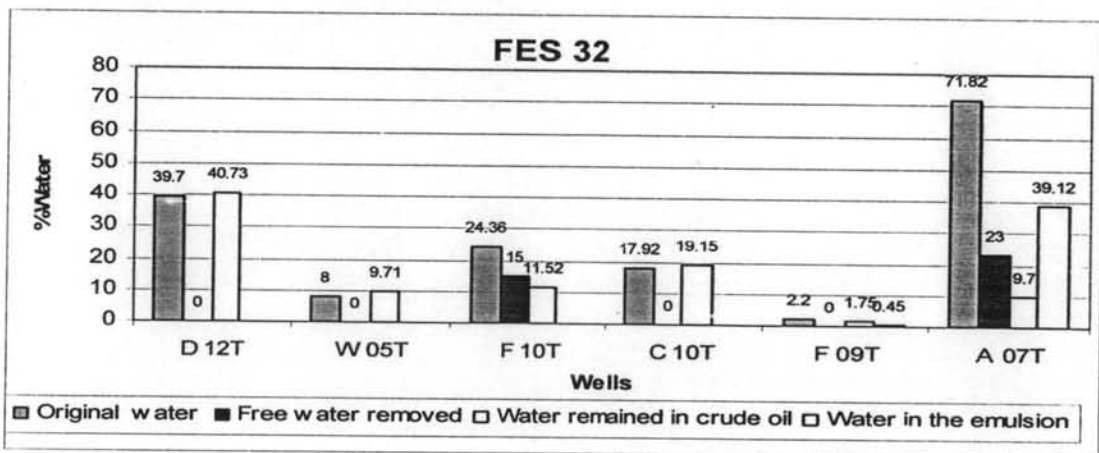
Figure 4.6 (a-c) (cont.) Water separation by bottle test using NP series of demulsifiers at 60°C.

4.2.2 Anionic Surfactants

4.2.2.1 *Fatty alcohol polyglycol ether sulfate, sodium salts*

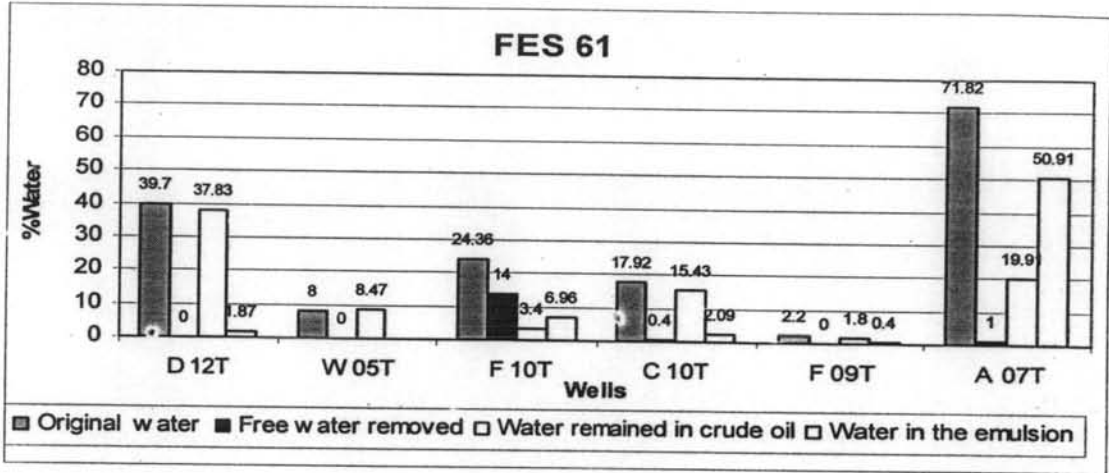
- FES Series

None of these series exhibited effective water separation. The results are shown in Figures 4.7 (a-d). These series seem to be an emulsifying agent because it increased the emulsion phase.

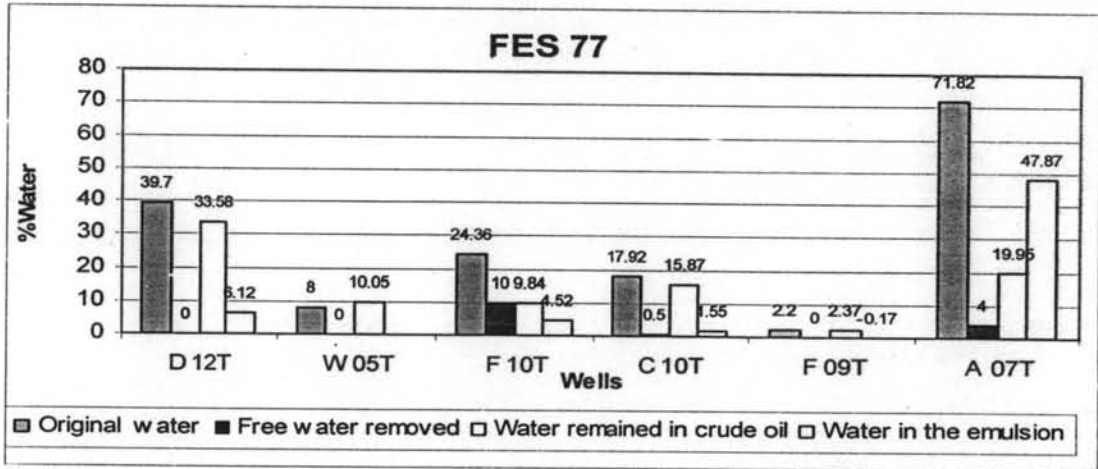


a

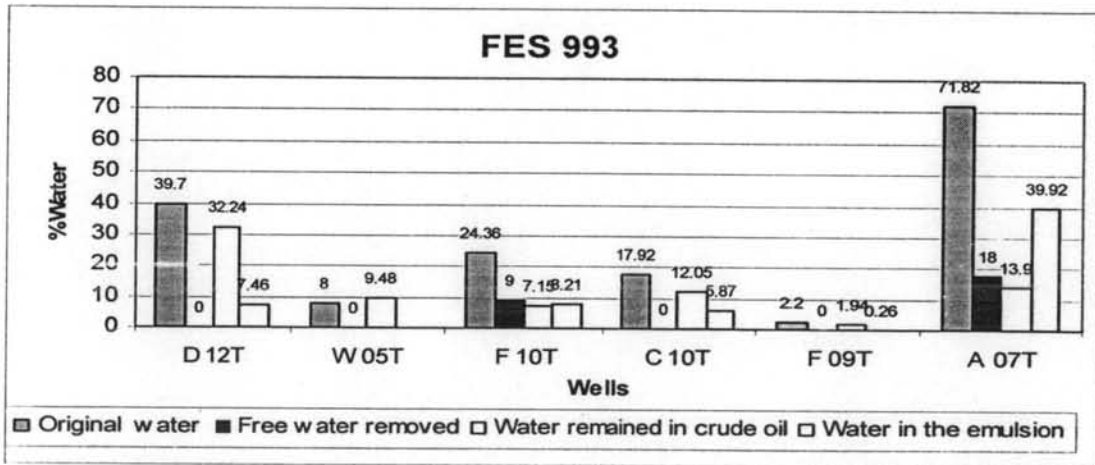
Figure 4.7 (a-d) Water separation by bottle test using FES series of demulsifiers at 60°C.



b



c



d

Figure 4.7 (a-d) (cont.) Water separation by bottle test using FES series of demulsifiers at 60°C.

-AFX Series

The demulsification efficiency of another group of fatty alcohol polyglycol ether sulfate (AFX series) are shown in Figures 4.8 (a-j). None of these showed good efficiency, except AFX 3070 worked the best for crude F 10T

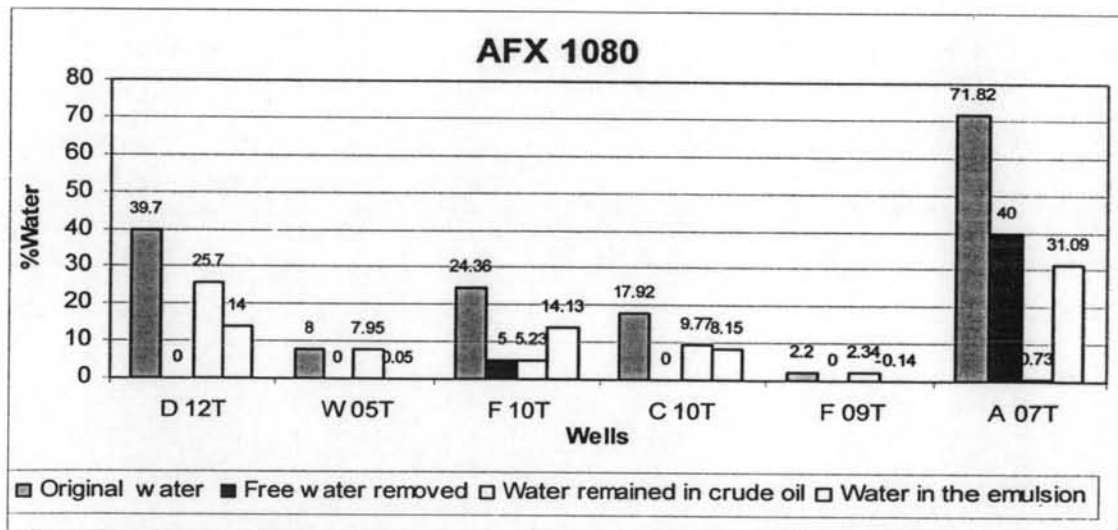
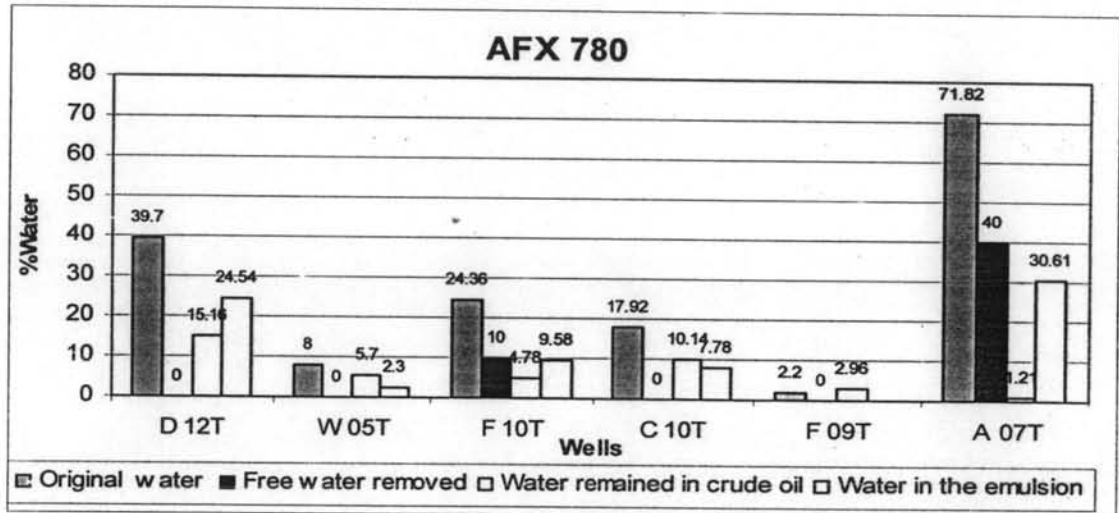


Figure 4.8 (a-f) Water separation by bottle test using AFX series of demulsifiers at 60°C.

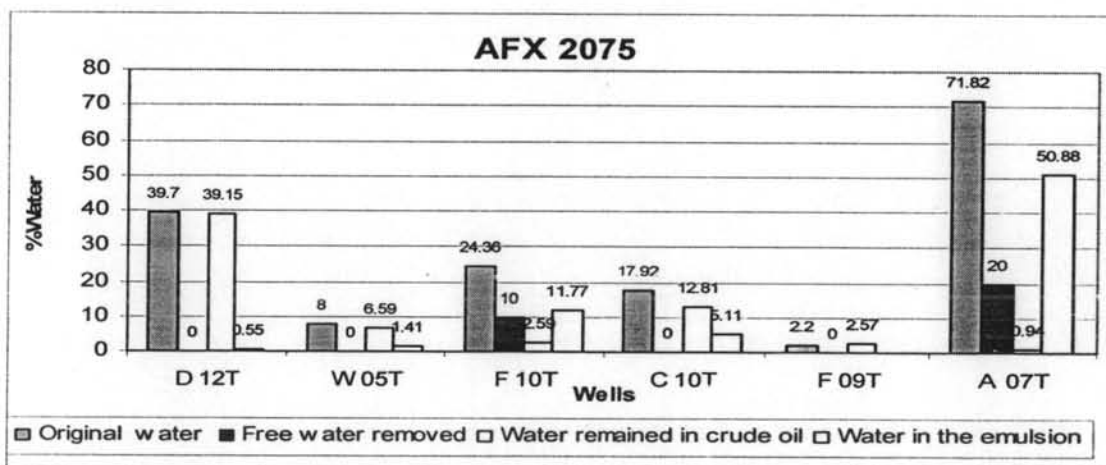
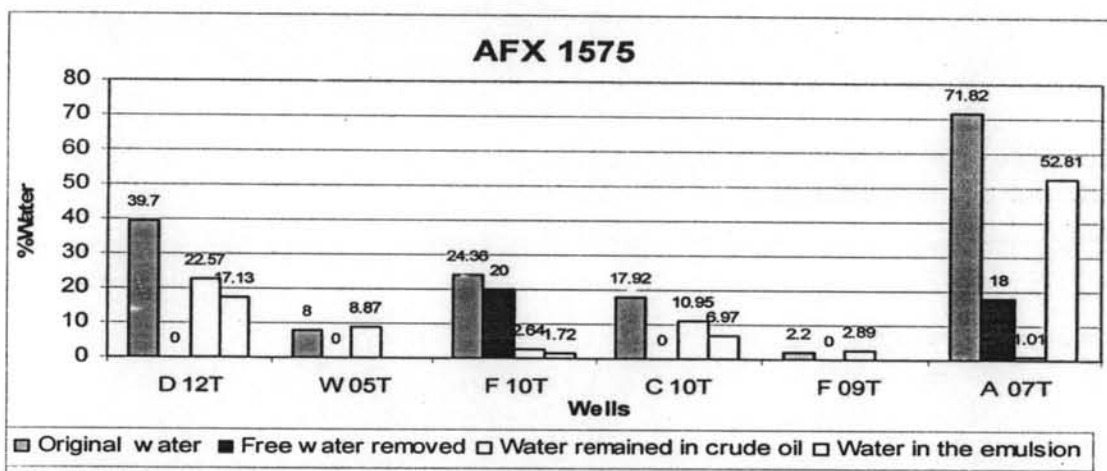
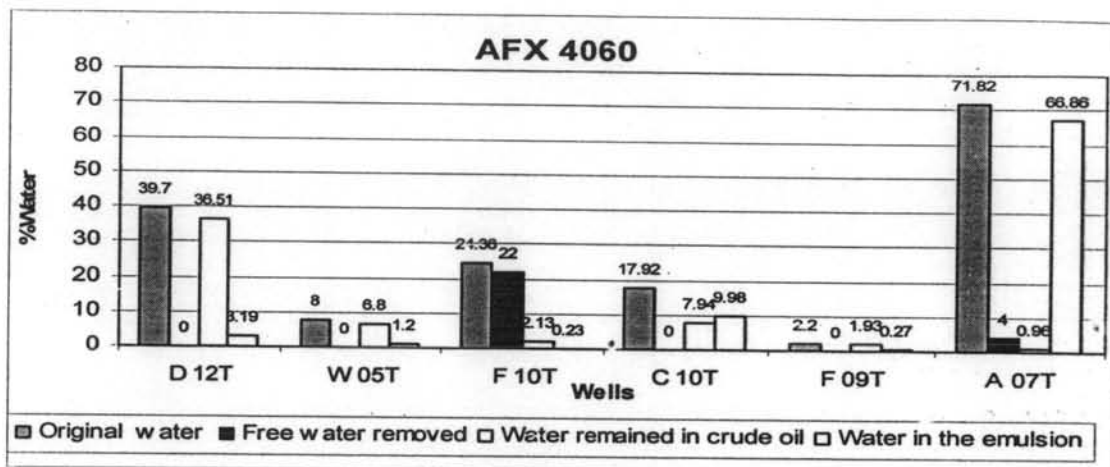


Figure 4.8 (a-f) (cont.) Water separation by bottle test using AFX series of demulsifiers at 60°C.

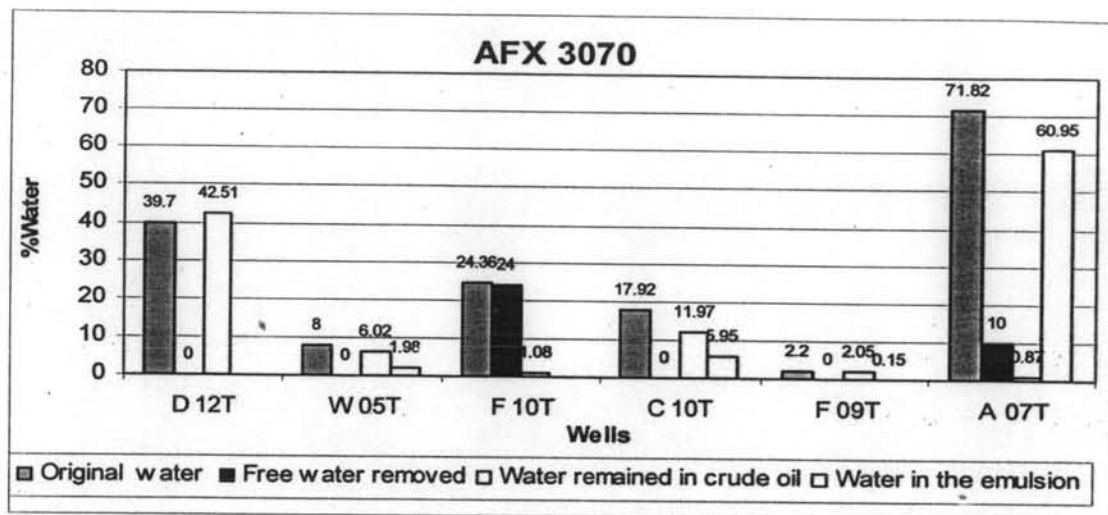


Figure 4.8 (a-f) (cont.) Water separation by bottle test using AFX series of demulsifiers at 60°C.

4.2.2.2 Sulfosuccinate Based

Figures 4.9 (a-c) show the results of demulsification of SUS series. None of these showed good water separation.

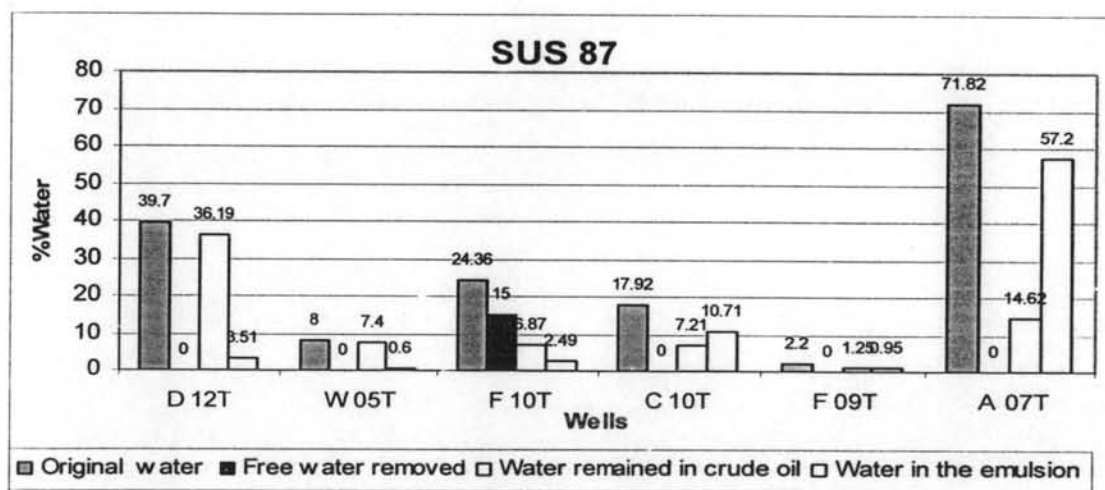


Figure 4.9 (a-c) Water separation by bottle test using SUS series of demulsifiers at 60°C

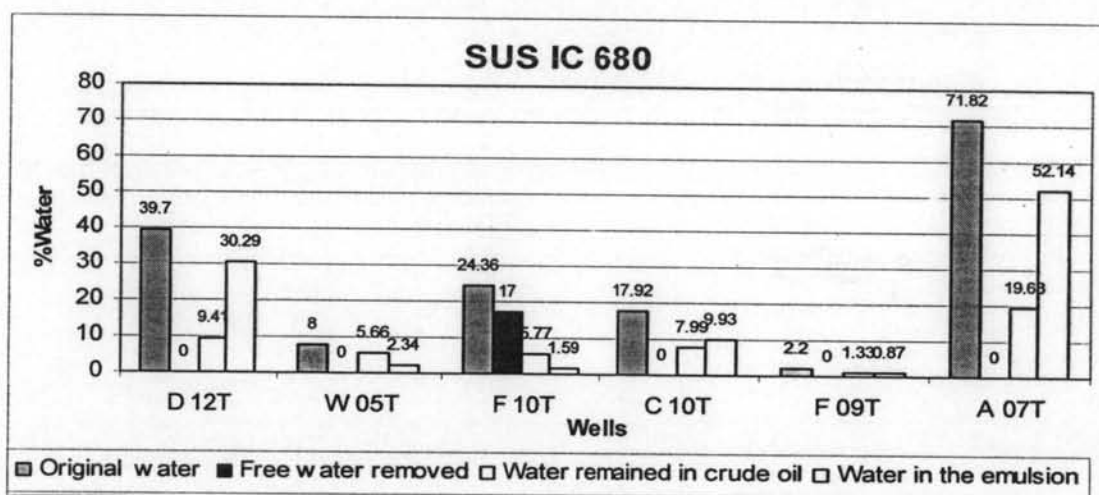
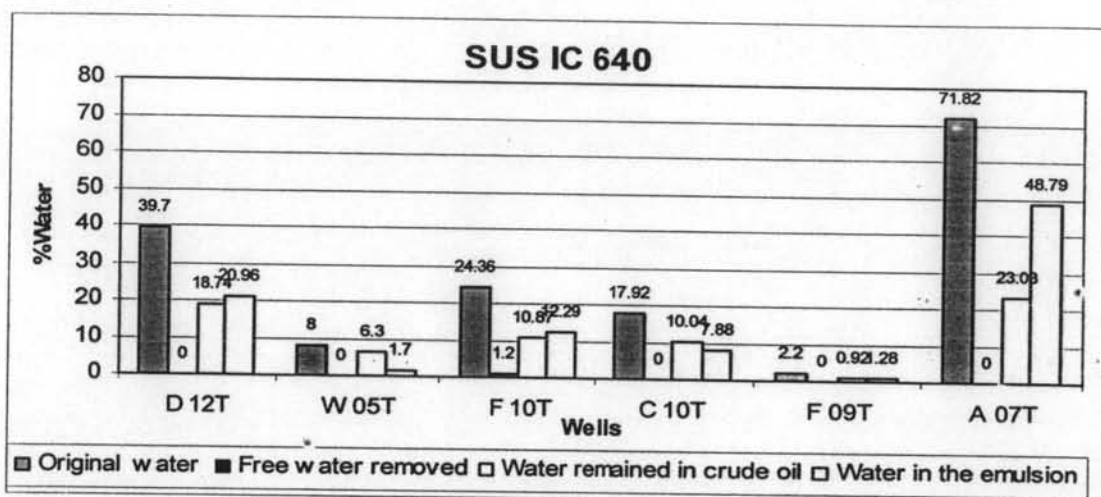


Figure 4.9 (a-c) (cont.) Water separation by bottle test using SUS series of demulsifiers at 60°C

4.2.3 Commercial Demulsifier

The PT 5135 commercial demulsifier was tested for its water removal efficiency. The results exhibited a slightly better efficiency in removal of free water for some crude. On the other hand, Teric 61 and Teric 87 could perform better for crude W 05T and C 10T. The result of PT 5135 is shown in Figure 4.10.

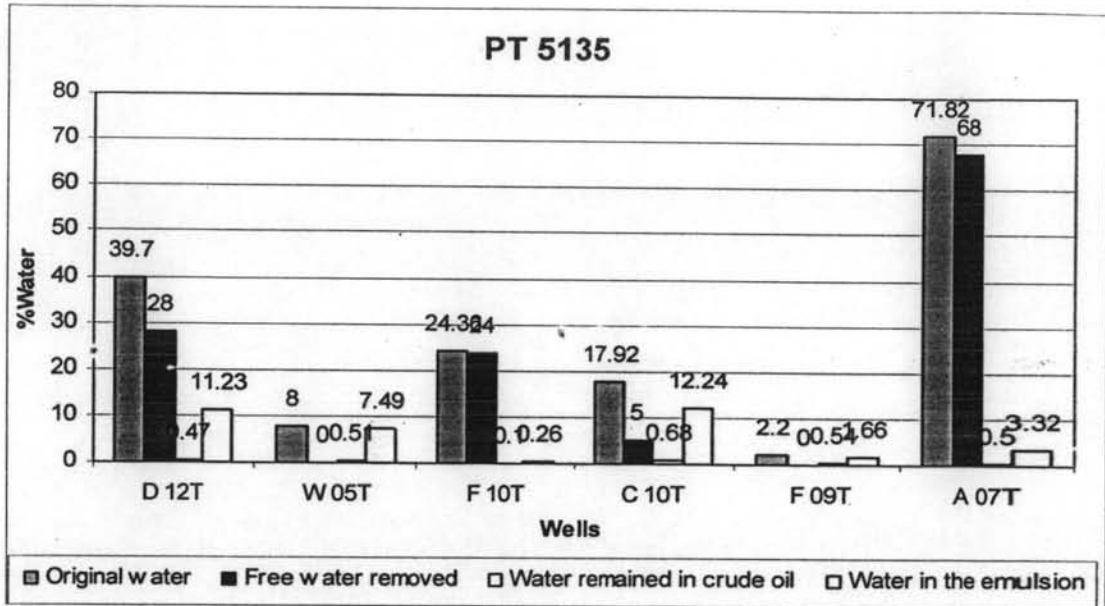


Figure 4.10 Water separation by bottle test using PT 5135 demulsifiers at 60 °C.

After screening all demulsifiers, we can preliminary choose the best demulsifier that represent from all groups and it is shown in Table 4.4. Nonionic surfactant, Terics 61 and 62 gave the best water removal from all crude samples, which water remaining in crude were mostly less than 0.5%. However, the free water removed was less than the original water and the mass balance of water indicated that there was water remaining in emulsion. The results also occurred with the commercial demulsifier (PT 5135). It is noted that the commercial demulsifier is generally formulated with many chemicals to crop with crude variations which are varied from field to field. The effects of various variables were studied with the preliminary screened demulsifiers.

Table 4.4 Summary of surfactant screening at 60°C

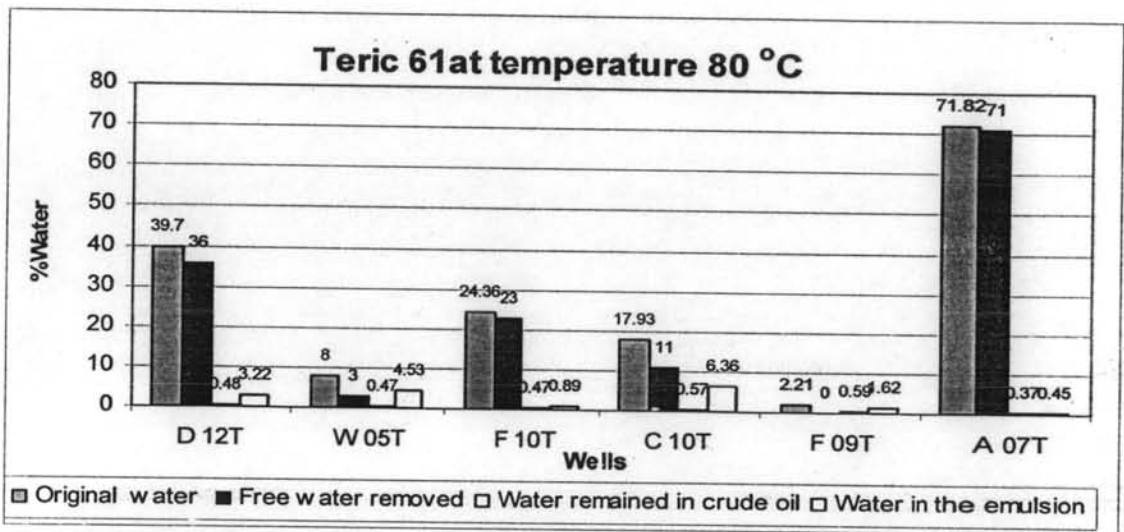
Demulsifier	Cloud Point (°C)	D 12T		W 05T		F 10T		C 10T		F 09T		A 07T	
		Original water 39.7%		Original water 8.0%		Original water		Original water		Original water 2.20%		Original water	
		% Water		% Water		% Water		% Water		% Water		% Water	
		Remove	Remaind in crude	Remove	Remaind in crude	Remove	Remaind in crude	Remove	Remaind in crude	Remove	Remaind in crude	Remove	Remaind in crude
Teric 61	16-18	20	0.5	0	0.47	11	0.2	18	0.25	0	0.89	61	0.59
Teric 62	22-24	6	0.34	0	0.42	7	0.44	8	0.37	0	0.17	67	0.41
Teric 87	6-8	2	0.78	2	0.45	18	0.57	2	0.59	0.6	0.8	48	0.42
NP6	Insolu ble	0	31.29	0	7.52	21	5.33	0	11.25	0	1.91	60	1.26
FES 32	-	0	40.73	0	9.71	15	11.52	0.5	19.15	0	1.75	23	9.7
AFX 780	-	0	15.16	0	5.7	10	4.78	0	10.14	0	2.96	40	1.21
AFX 3070	-	0	42.51	0	6.02	24	1.08	0	11.97	0	2.05	10	0.87
SUS 87	-	0	36.19	0	7.4	15	6.87	0	7.21	0	1.25	0	14.62
PT 5135	-	28	0.47	0	0.51	24	0.1	5	0.68	0	0.54	68	0.50

4.3 Effects of Temperature, Salinity, pH, and Solvent

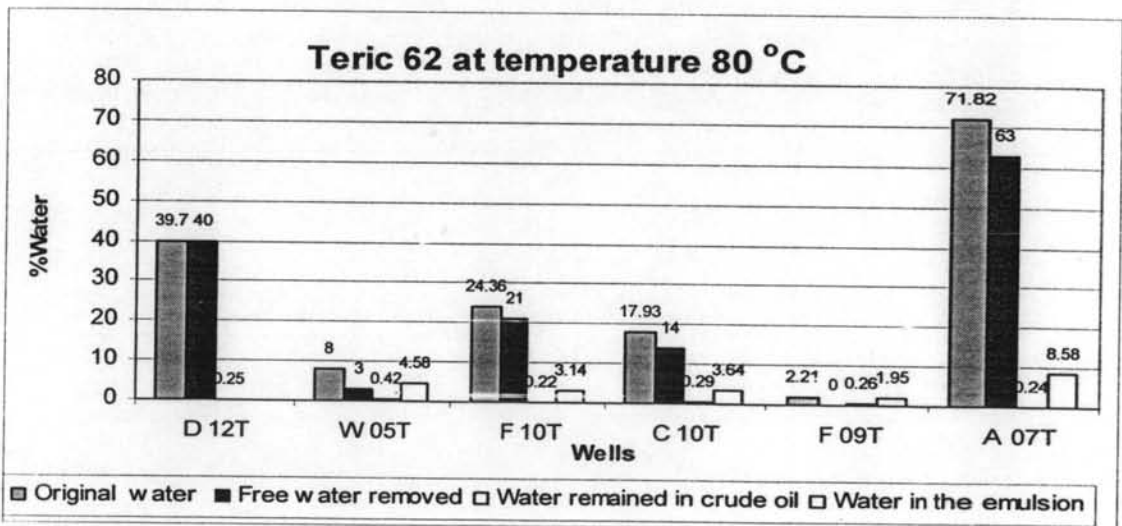
4.3.1 Effect of Temperature

The best nonionic surfactants, Terics 61 and 62 were selected for studying the effect of temperature. Figure 4.11 (a-f) demonstrates the effect using 1000 ppm demulsifier. The result revealed that demulsification efficiency of the demulsifier increases with increasing the temperature. At 40 °C there was no water separated at all. At 60 °C the water in crude was separated to meet the required level (below 0.5%), while at 80 °C, the most water was separated from crude and emulsion phases. This effect is attributed to the change of interaction between demulsifier-oil and probably asphaltenes at the interfacial film. Asphaltenes are considering as the natural surfactants that stabilize the water in oil emulsion. Increasing the temperature results in a decrease of the interfacial shear viscosity, this effect can results in an

increase of the rate of drainage. This effect was also explained by Bloster and Little (1980), the viscosity of the continuous phase would be expected to have a major effect on the rate of demulsification since it would affect both collision frequency and sedimentation velocity of the coalesced droplets. In other words, heat accelerates the emulsion breaking process. Increase temperature results in an increased density difference between two liquids. Eventually the phase separates.

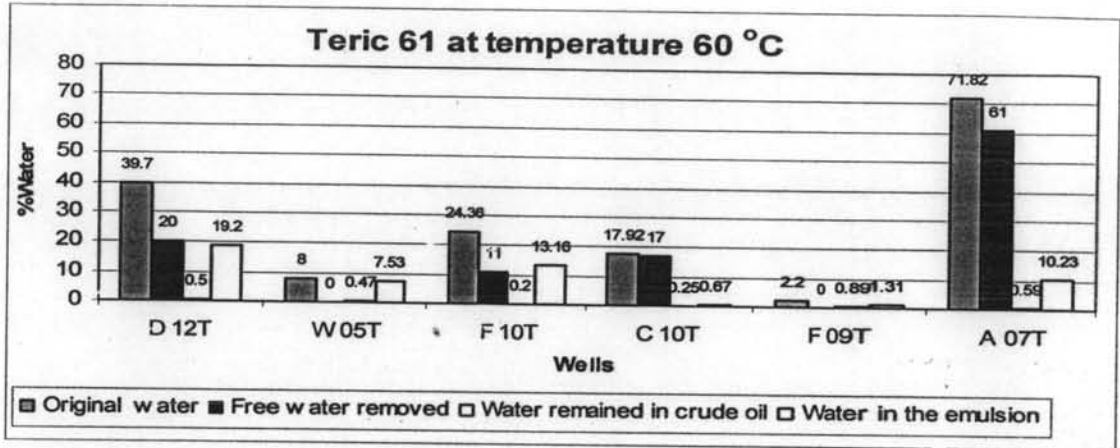


a

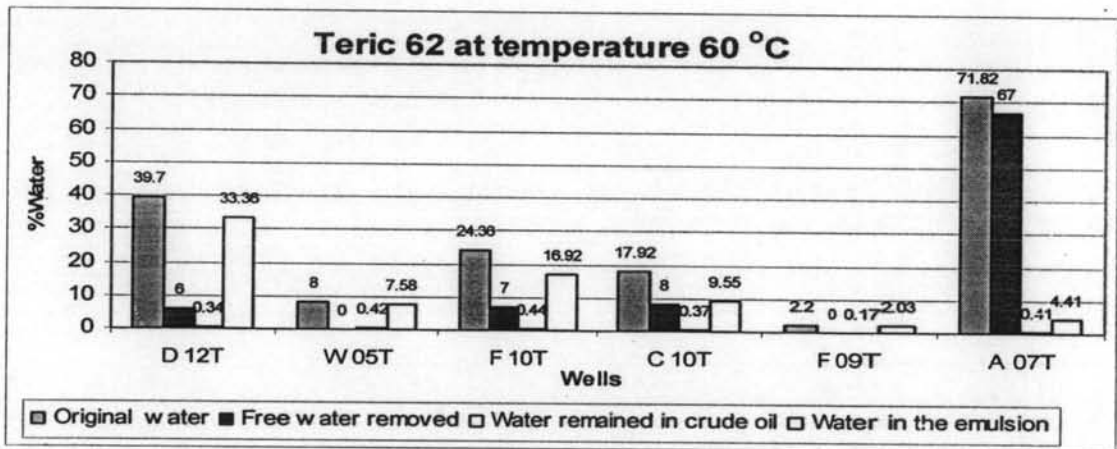


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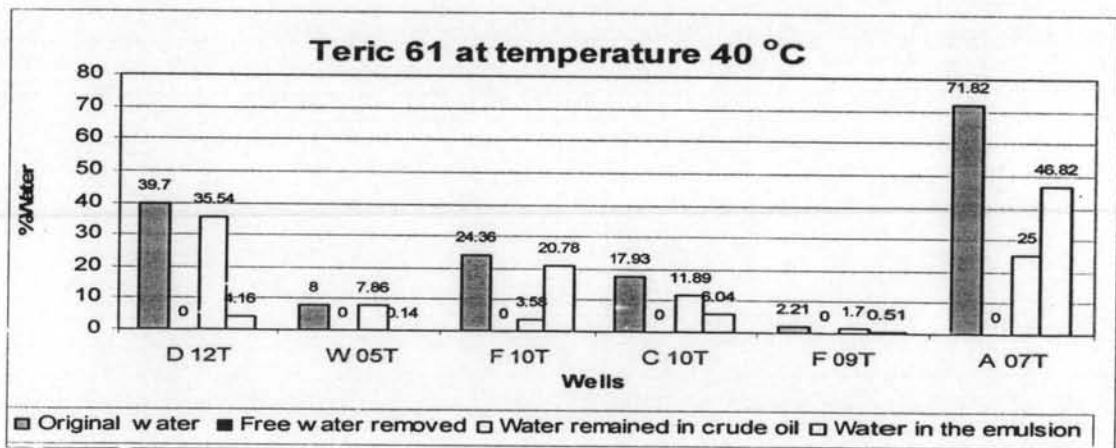
Figure 4.11 (a-f) Demulsification of Teric 61 and Teric 62 at 80, 60, and 40°C.



c



d



e

Figure 4.11 (a-f) (cont.) Demulsification of Teric 61 and Teric 62 at 80, 60, and 40°C.

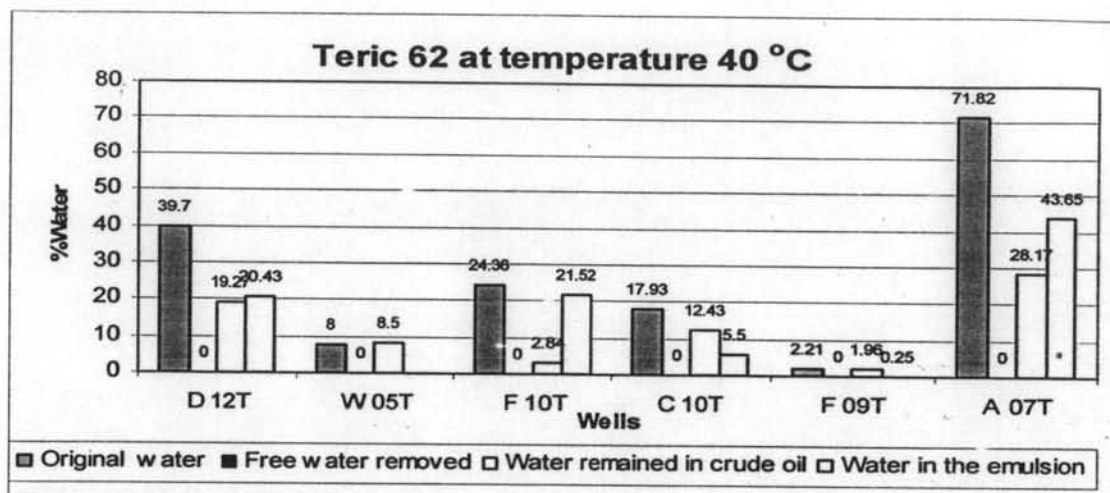


Figure 4.11 (a-f) (cont.) Demulsification of Teric 61 and Teric 62 at 80, 60, and 40°C.

4.3.2 Effect of Salinity

Salinity background of crude samples were analyzed for K^+ , Li^+ , Na^+ , Ca^{2+} , Mg^{2+} , and Fe^{2+} . Table 4.5 presents the results of alkali ions in each well. Therefore the salinity from the formation probably had less effect on the efficiency of demulsifiers. Most of the cation present in crude oil was sodium and the highest concentration (D 12T) was less than 0.5M.

Figure 4.12 illustrated the dependence of the demulsification efficiency at 1000 ppm of Teric 61 with the salinity solution from 0.0-1.0 M at 60 °C. The curves show the same trend as increasing the concentration of NaCl. When it was compared with 0.0 M salinity solution (Teric 61 in aqueous solution), the amount of free water separated out was less than the 0.0 salinity solution. Therefore addition of salinity solution into nonionic system had no effect on the demulsification.

Table 4.5 Alkali salt contaminated in the water phase of crude oil

wells	Na (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Li (mg/L)	Fe (mg/L)
D 12T	10,261	331	50	3	0	0
W 05T	1,428	400	86	8	0	0
F 10T	1,666	60	0.83	5	0	0
C 10T	5,000	1425	137	12	0	0
F 09T	2,500	475	62	14	0	0
A 07T	2,142	774	65	12	0	0

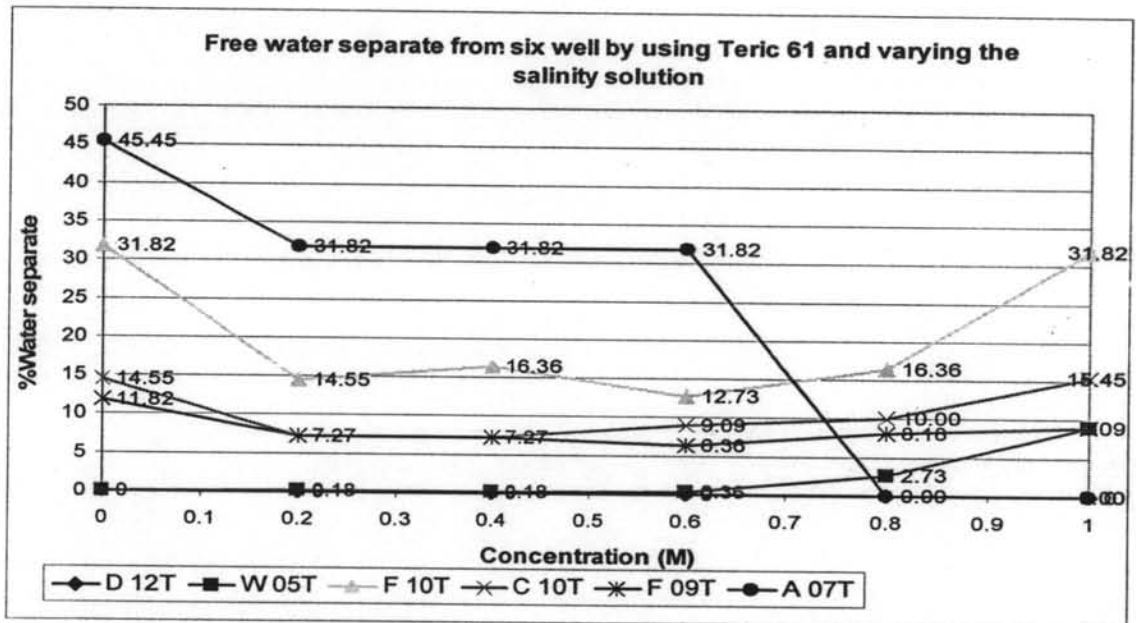
**Figure 4.12** Salinity effects on Teric 61 demulsifier by varying salinity concentration from 0.0-1.0 M.

Figure 4.13 showed the results of the AFX 780 efficiency with varying salinity concentration. The results showed that salinity increase demulsification efficiency of AFX 780 for most samples except D12T.

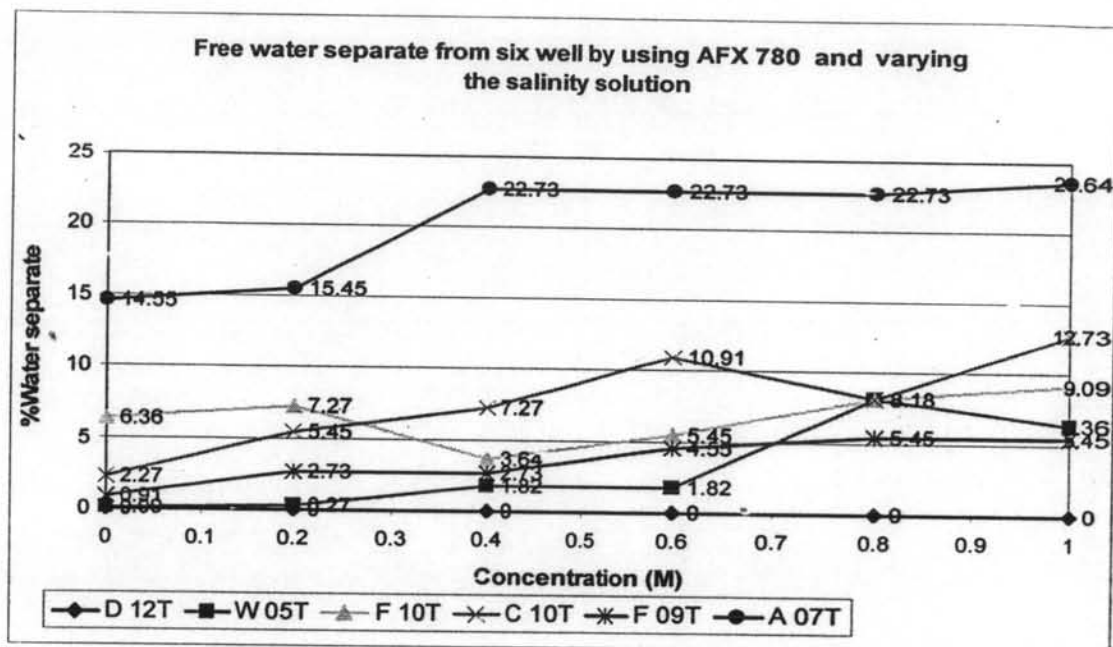


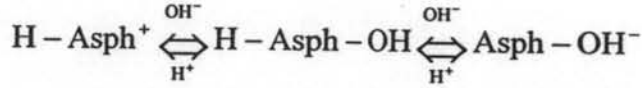
Figure 4.13 Salinity effects on the AFX 780 demulsifier by varying salinity concentration from 0.0-1.0 M.

4.3.3 Effect of pH

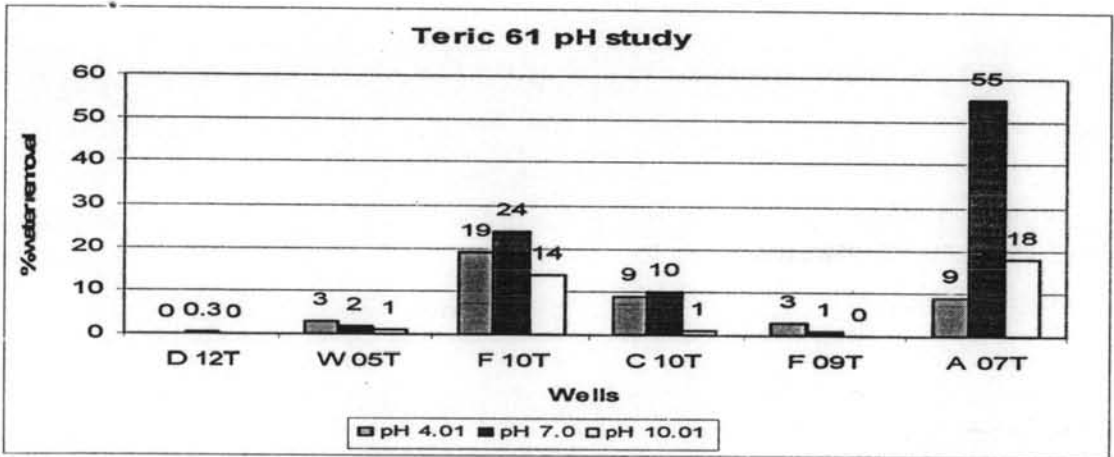
The pH values in aqueous phase were measured and the results called background pH were in the range of 8-9. To study the effect of pH by using buffer solution at three different pH values of 4.01, 7.00, and 10.01 the buffer solution was injected along with the 1000 ppm demulsifier to the crude oil. The percentages of water removal by all demulsifiers are presented in Figures 4.14 (a-d). The results after applied buffer pH 4.01 are almost the same as pH buffer 7.00 which is the best pH value for demulsifiers efficiency while pH 10.01 exhibited less effect. Because the final pH was checked and found that the pH of all crudes changed to pH around 7-8, 7-8 and 9-10 after the corresponding buffer solution 4.01, 7.00, and 10.01 were added. The best water separation with nonionic surfactant was around pH 7.

The maximum demulsification efficiency from nonionic demulsifiers were obtained at the neutral pH value, however its decrease with increasing acidity or alkalinity. The experiment can be confirmed by the Kokal (2005) paper. This is because of ionization effect (i.e. association / interaction of ion present in the brine with the asphaltenes). Abdel-Azim (2002) explained that asphaltenes adsorbed at the

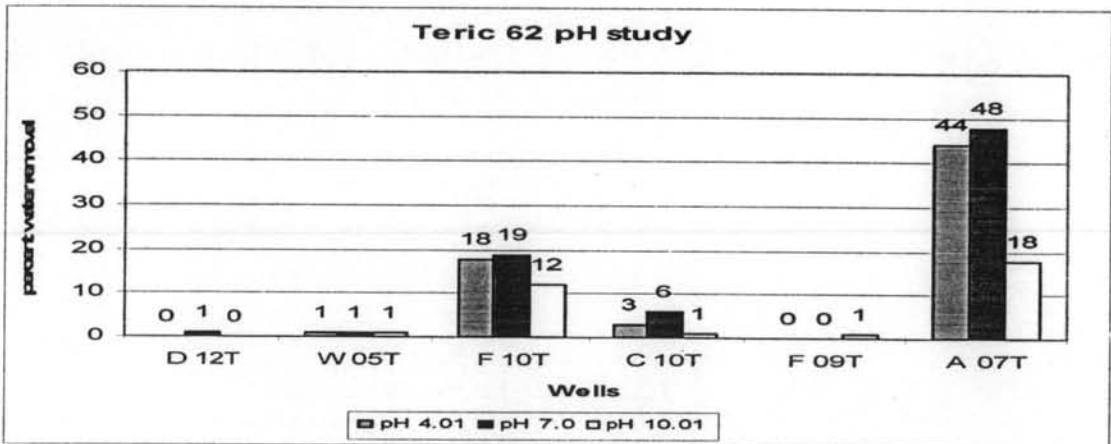
interface behave amphoteric, and the water droplets will acquire a negative charge in basic medium and a positive charge in acidic medium due to ionization equilibrium of asphaltenes according to the following equation.



It is recognizing that surface charges on the water droplets interface cause electrostatic repulsion. Meanwhile, acidic or alkaline medium will enhance emulsion stability by using electrostatic force to exhibit the coalescence.

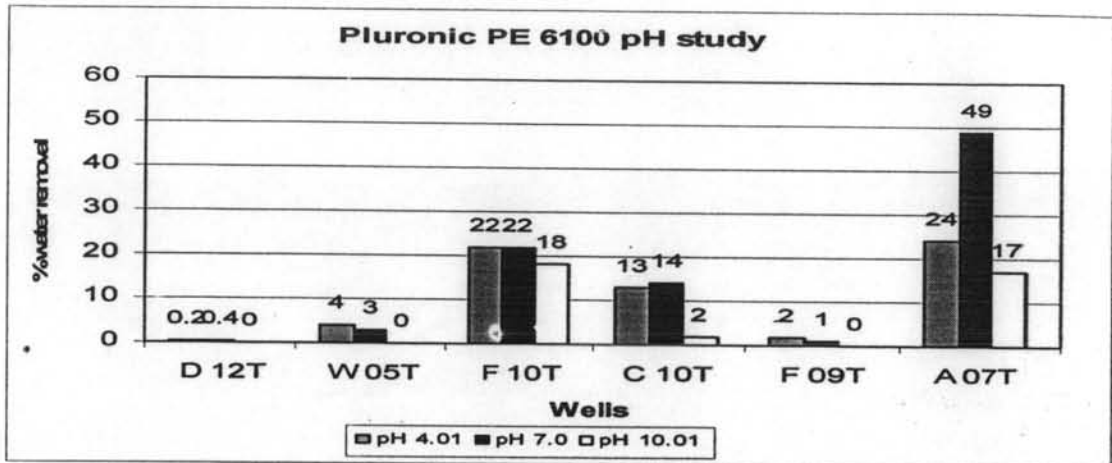


a

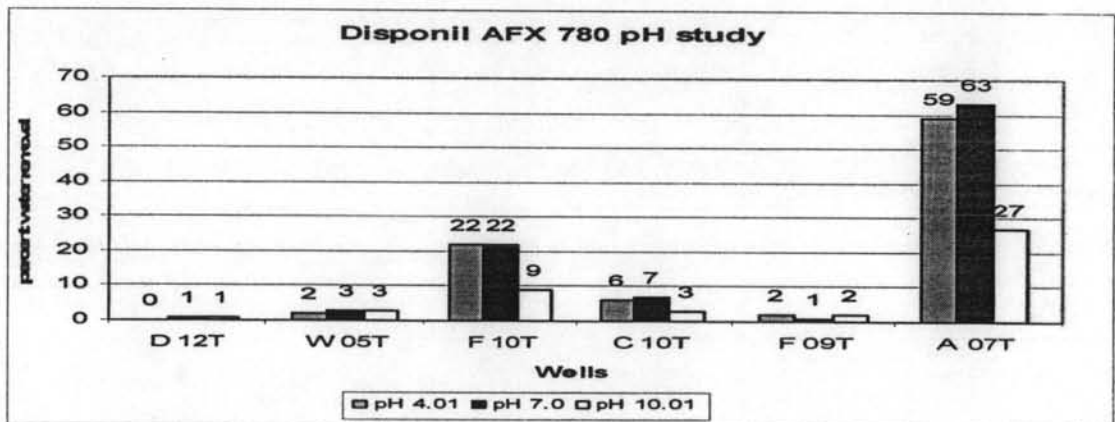


b

Figure 4.14 (a-d) The effect of pH at 60°C and 1000 ppm on Teric 61, Teric 62, Pluronic PE6100, and AFX 780 respectively.



c



d

Figure 4.14 (a-d) (cont.) The effect of pH at 60°C and 1000 ppm on Teric 61, Teric 62, Pluronic PE6100, and AFX 780 respectively.

4.3.4 Effect of Solvents

Figure 4.15 shows preliminary study of the influence of the type of solvent on demulsification efficiency of Teric 61. From the results, it seemed that xylene and toluene were the most efficient solvent causing the highest water separation (express as % water separated). Addition of water to the crude that already contained water could improve water separation. Thus, water is one of the parameter that needed to be properly set in the crude before applying a separation method.

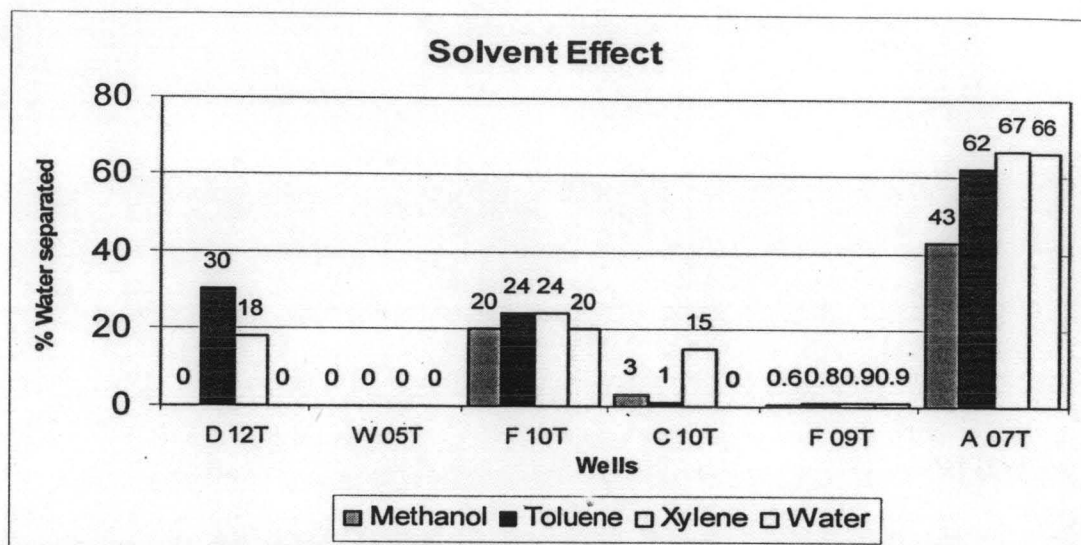


Figure 15 Shown the solvent effect on the demulsification efficiency of each well.

4.4 Effect of Demulsifiers on Mixed Crude Oil

The proportion of crude oil was 1:1:1:1:1 (Appendix I). After blending, the water content was 34.03%. Figure 4.16 exhibited the demulsification efficiency on the blended crude oil. Teric 61, Teric 62, AFX 780, Pluronic PE6100, and mixed demulsifiers (Teric 61 and Pluronic PE6100) were selected about the same as that of the single demulsifier. The results showed that mixed demulsifiers were the best since it removed water up to 32% out of 34% and the water remaining was lower than 0.5% as shown in Figure 4.17.

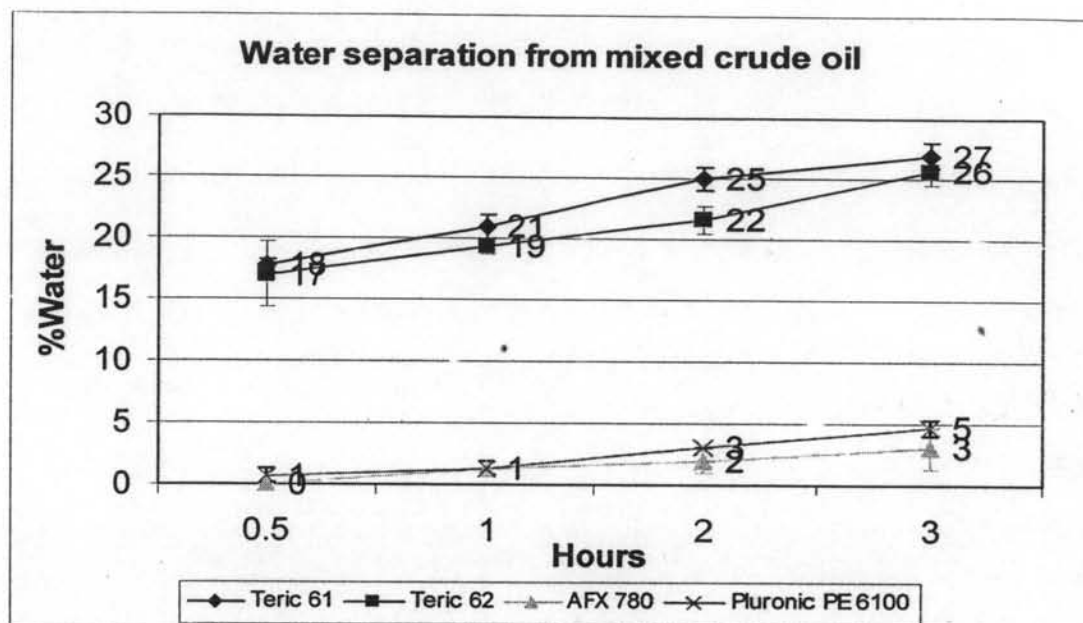


Figure 4.16 The percentage of water separated from mixed crude oil by using Teric 61, Teric 62, AFX780, Pluronic PE6100, and mixture of Teric 61 and Pluronic PE 6100.

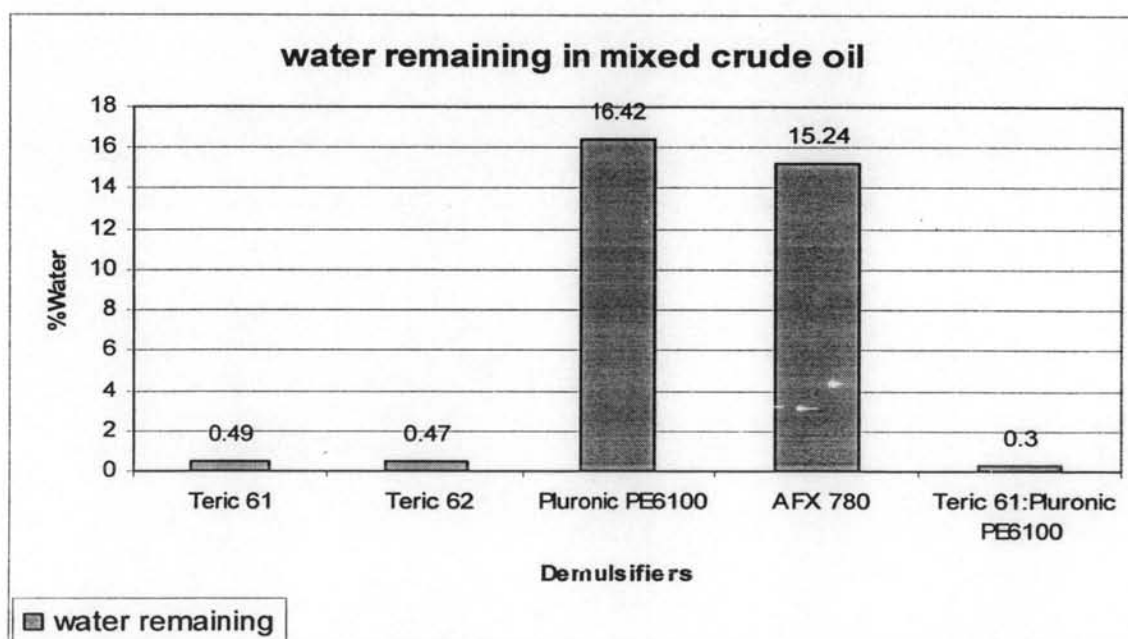


Figure 4.17 The water remaining in mixed crude oil after treated with different demulsifiers.