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THE EFFECT OF SURFACTANT (SODIUM LAURYL SULPATE) AND DEMULSIFIER (HEXANE) ON CRUDE OIL EMULSION TREATMENT

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Abstract— Crude oil emulsions pose significant problems to petroleum production and processing and as such have received serious attention towards providing lasting solutions to alleviate these production problems. The use of surfactants and demulsifiers has proven to be industry's most recognized method for the treatment of crude oil emulsions. In this study a laboratory investigation was carried out in order to determine the effect of surfactant, Sodium Lauryl Sulphate (SLS) and demulsifier (Hexane) on emulsion treatment at different concentrations. Two samples of crudes (IMOR3-023L and AGBDI-013L) were used with Sodium Lauryl Sulphate (SLS) as surfactant, Hexane as the demulsifier and Toluene as a stabilizer to form an emulsion. For each crude sample, eight (8) samples of emulsions were formulated with varying volume concentrations of the water, demulsifier and surfactant. For all the samples, Toluene (stabilizer) was kept constant while the demulsifier (Hexane) is kept constant and surfactant (SLS) varied for the first test. For the second test, the Hexane (demulsifier) was varied and SLS (Surfactant) was constant. The result shows that when Toluene and Hexane were kept constant with SLS varied, sample A has significant increase in the volume of water separated from 13ml to 16ml for range of 1hr to 5hrs and Sample B with volume of water separated from 3.8ml to 10.1ml for range of 1hr to 5hrs. Similarly, sample C and D recorded significant increase also when Toluene and SLS was kept constant with Hexane varied. Sample I and sample J has significant increase in the volume of water separated from 3ml to 9.9ml and 12ml to 12.9ml for range of 1hr to 5hrs. In general, varying the volume of Hexane has higher percentage of water recovered and separated than SLS. This research has shown the effectiveness of chemical method for crude oil emulsion treatment and should be adopted as separation will be fast and less expensive.

Keywords— Demulsifiers, Hexane, Sodium Lauryl Sulphate, Stabilizers, Surfactant

I. INTRODUCTION

Water in Oil and Oil in water emulsion is a common problem encounter during and after crude oil production and requires cost effective separation techniques to meet market specification and discharge standard. Oil and water mixtures are usually not stable even when their droplets tends to merge together and requires an emulsifier to stabilize the emulsion (Pichot, 2012). The difficulty of separating water-oil emulsion mixture has been a subject of study for decades. Several chemical and physical methods have been proposed by many studies for separating emulsion mixtures with the use of surfactants standing atop as a result of its efficiency to separate oil molecules from water molecules at their boundary interface with economy (Siti-Nuurul-Huda, 2010).

Demulsifiers which are molecules that separate oil from water at low concentrations are important in breaking an emulsion system (Al-sabagh et al, 2011). The principle of demulsification by physical methods (separation/breaking of emulsions) is based on conductive heating aimed at breaking the oil-water interface via surface tension reduction and by centrifuging aimed at shaking off the less dense specie from the mixture. However, where there are remarkable concentrations of polar molecules with hydrophilic and hydrophobic ends, surface tension reduction by conductive heating are generally insufficient for breaking the crude oil emulsions. In this case, specially formulated complex organic compounds are generally applied or argument with physical methods (Raymond, 2003). These organic compounds are generally called surfactants.

During treatment, it is often necessary to keep the emulsion stable. This can be achieved by combining surfactants and colloidal particles. Surfactants are generally amphiphilic in nature and as a result will have a natural affinity for the oil-water interface which they eventually attack thereby reducing the oil-water interfacial tension and the energy required for the formation of emulsion. These adsorbed



surfactant molecules at the interface act as electrostatic or steric barriers against droplet coalescence and increase the emulsion stability (Megahn, 2001). The extent of the hydrophilic-hydrophobic balance provided by the surfactant molecules will determine the resulting type of the emulsion being formed-water-in-oil or oil-in-water emulsion.

The colloidal particles used in emulsion stabilization are not amphiphilic. However, they are partly wettable in each of two immiscible phases which eventually favors the location of liquid-liquid interface (Golemanov, 2008). They do not like surfactants reduce the oil-water interfacial tension, but they are strongly adsorbed at the oil-water interface. This adsorption process is slow and more often than not, need to be enhanced.

Experimental investigation of the rheology and stability behavior of surfactant stabilized water-in-oil-emulsion, showed that the behavior and stability of surfactant stabilized crude oil emulsion depend on viscosity, total acid and base number (Israel, 2016) and (Schubert & Armbruster, 1992).

Previous investigation was performed in order to predict water-in-oil emulsion coalescence from surface pressure isotherms. A droplet of a solution of asphaltenes, *n*-heptane and toluene was formed and aged at the tip of a capillary in an aqueous medium. Irreversibly adsorbed films were observed to form rapidly at all asphaltene concentrations and rigid films form least rapidly at intermediate asphaltene concentration (10 kg/m³). A “phase change” from a compressible film to an almost incompressible film occurred upon compression in most cases (Patricia, 2006).

The breaking of oil-water emulsion for improvement of oil recovery operations in the Niger delta oilfields has been investigated in which selected cationic surfactants were prepared and used to investigate their breaking potential on emulsions during enhanced recovery operations. It was observed that the surfactants were effective in separating oil-water emulsions expected during a surfactant/polymer (SP) process for improved oil recovery. (Ijogbemeye et al, 2012).

The evaluation of the actual effect of surfactants on crude emulsion systems is relevant if the effective use of surfactants needs to be achieved. The surfactants use of oil-water emulsions produces result based on the type of surfactant, operating conditions and the properties of the emulsion system under consideration (Mazus, 2013). A number of analytical models based on modeling and simulation have been present for analyzing the effect of surfactants on crude oil emulsions. However, the major limitation of these analytical models is assumptions that did not properly describe the actual operation environment for surfactants application on emulsions. Although, these models are quicker and predictive in nature compared to laboratory analysis, the latter has been adopted as the most effective method for investigating surfactant effect on emulsion crude.

According to Orji and Duhu (2012), there are still many prevalent issues in the selection of demulsifiers for crude oil

treatments. This is because, crude oil of different API gravity respond differently to several demulsifiers. In this study, laboratory investigation of the effect of surfactants and demulsifiers on crude oil emulsion treatment has been carried out to determine how different surfactants and demulsifier affect the volume of water recovered from the emulsion at varying operating conditions, giving rise to maximum recovery.

II. MATERIALS & METHOD

Experimental procedures were carried out to investigate the effect of demulsifiers and surfactants on emulsion treatment. Two samples of crudes (IMOR-023L and AGBDI-013L) were used with Sodium Lauryl Sulphate (SLS) as surfactant and Hexane as the demulsifier. Toluene was used as a stabilizer in the process. For every crude sample, eight (8) samples of emulsions were formulated with varying volume concentrations of the water, demulsifier and surfactant. The treatment potential of the demulsifier and the surfactant was evaluated by the volume of water recovered. The detailed description of the laboratory procedures and the materials/apparatus are presented.

A. Materials and Apparatus

In this study, the materials/apparatus used include: Two (2) different crude oil samples, distilled water, Toluene (used as a stabilizer), Sodium Lauryl Sulphate, SLS (surfactant), Hexane (demulsifier), sets of beakers, 100ml measuring cylinder, 25ml pycnometer, Red Wood Viscometer, weighing balance, pH meter, air coolers and wash bottles.

B. Experimental Procedures

Measuring cylinders and beakers were washed and dried. 100ml graduated measuring cylinder were labeled for different samples and were filled with the following volume ratio of water to crude oil: 15:20, 14:20, 13:20 and 12:20 respectively. Known sample of Toluene was added for the stability of the emulsion with different concentrations of surfactants (SLS) ranging from (1-4 ml) at constant volume of demulsifier (hexane). The sample mixture was agitated for about 2-5 minutes at room temperature and the volume of separation was observed on hourly basis for 5 hours. The above procedures were repeated for each of the samples with the volume of SLS kept constant and hexane varied from 7ml to 10ml. Emulsion formulation Sample preparation volume and composition is presented in Table 10 to Table 13 of Appendix A.

II. RESULTS AND DISCUSSION

The results of the experiment performed in this study are presented in this section and discussions are based on the findings/results obtained in order to explicitly explain the principle behind the observed behavior/trend and property

changes. In Tables (1-4), the volume of water separated on hourly basics is presented for each case and test condition.

Table 1: Hourly Water Recovery of AGBDI – 013L Emulsion (Hexane and Toluene Volumes kept constant)

Time	1 hr	2 hrs	3 hrs	4hrs	5 hrs
SAMPLE A	13 ml	14 ml	14.5ml	15ml	16.0 ml
SAMPLE B	3.8 ml	6.5 ml	8.3 ml	9.9ml	10.1 ml
SAMPLE C	2.5 ml	4 ml	5.9 ml	7 ml	8.0 ml
SAMPLE D	14 ml	14.7ml	15.0ml	15.2ml	15.5 ml

Table 2: Hourly Water Recovery of IMOR3-023L Emulsion (Toluene and Hexane constant)

Time	1 hr	2 hrs	3 hrs	4hrs	5 hrs
SAMPLE E	7.9 ml	8.5 ml	9.0 ml	10ml	10.8 ml
SAMPLE F	12.9ml	13.0ml	13.1ml	14 ml	14.5 ml
SAMPLE G	7.0 ml	8.0 ml	9.0 ml	9.9ml	10.0 ml
SAMPLE H	6.5 ml	8.9 ml	9.9 ml	10ml	10.1 ml

Table 3: Hourly Water Recovery of IMOR3-023L Emulsion(Toluene and SLS kept constant)

Time	1 hr	2 hrs	3 hrs	4hrs	5 hrs
SAMPLE I	3.0 ml	5.0 ml	8.0 ml	9.0 ml	9.9 ml
SAMPLE J	12. ml	12.5ml	12.6ml	12.8ml	12.9 ml
SAMPLE K	4.0 ml	6.0 ml	7.0 ml	9.0 ml	10.0 ml
SAMPLE L	3.9 ml	4.9 ml	5.0 ml	7.1 ml	8.9 ml

Table 4: Hourly Water Recovery of AGBDI – 013L Emulsion (SLS and Toluene Volumes kept constant)

Time	1 hr	2 hrs	3 hrs	4hrs	5 hrs
SAMPLE W	9.0 ml	11.2 ml	12.5ml	13.0ml	13.0ml
SAMPLE X	11.0ml	11.9 ml	12.1ml	12.2 ml	12.5ml
SAMPLE Y	11.0 ml	13.2 ml	14.0ml	14.1 ml	15.0ml
SAMPLE Z	10.8 ml	13.0 ml	13.2ml	14.0 ml	14.5ml

It can be observed that for samples A and D (Table 1), a significant amount of water was separated after 10minutes (9ml and 10 ml respectively). After 1 hour more water was separated (13 ml and 14 ml respectively). It is also noted that sample A and D achieved a higher volume of separation than sample C and D where the quantity of SLS was 1ml and 4ml respectively. The maximum volume of separation occurred at sample D in which the initial volume of water added to form the emulsion was 12ml and the volume of water separated from the sample was 15ml. This was achievable when the volume of SLS used was 4ml (at its highest). The extra volume of water separated was due to the fact that the crude contains water. The exact volume of water added to form the emulsion sample F was the volume of water separated at the end of the 5 hours interval, while for the other samples (E,G,H) in Table 2, significant increase occurred in

the volume of water separated at the end of the 5hrs interval but they were not able to recover the volume of water added to form the emulsion. Since for both crude samples the volume of hexane and toluene were kept constant at varying condition of SLS, it therefore indicates that the effect of surfactant on the treatment of crude oil emulsion is a function of emulsion type and the properties of the crude.

The results in Tables (3-4) were generated under a test case of constant SLB and Toluene. The results show that increase in the demulsifier (Hexane) increased the volume of water separated, this is seen in sample J where maximum volume of water was separated as compared to Samples(I,K,L) where significant increase in volume of water separated was noted. Hence the higher volume of demulsifier (Hexane) used when surfactant(SLS) and stabilizer (Toluene) are kept constant the more effective the maximum volume of water separated. The result shows that maximum volume of water separated was evident in sample Y while sample W,X and Z showed significant increase as the volume of demulsifier (Hexane) was increased at constant Toluene and SLS.

Figures 1 to 4 shows in detail the volume recovered with respect to time.

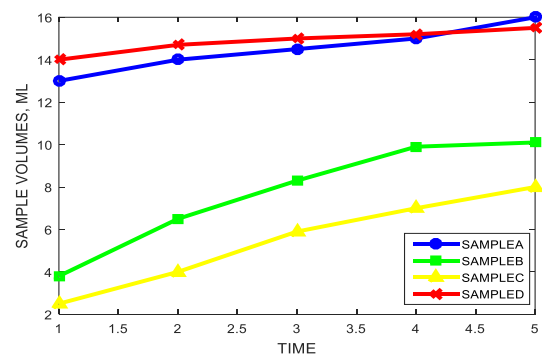


Figure 1: Water Volume Recovered from each Sample for AGBDI – 013L Emulsion (Hexane and Toluene Volumes kept constant)

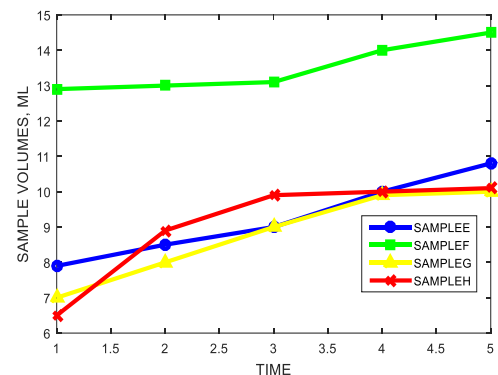


Figure 2: Water Volume Recovered from each Sample for (IMOR3-023L) Emulsion (Hexane and Toluene Volumes kept constant)

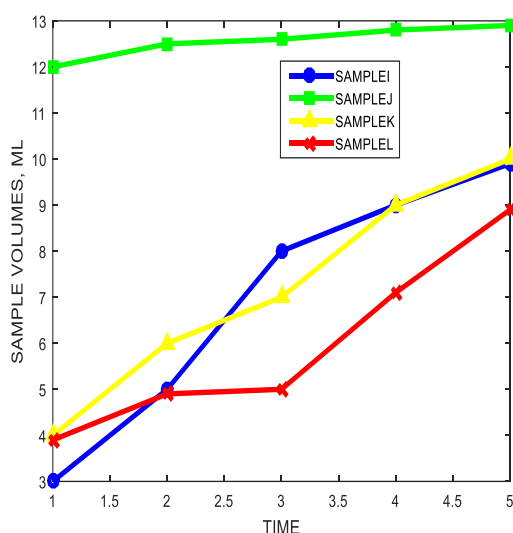


Figure 3: Water Volume Recovered from each Sample for (IMOR3-023L) Emulsion (SLS and Toluene Volumes kept constant)

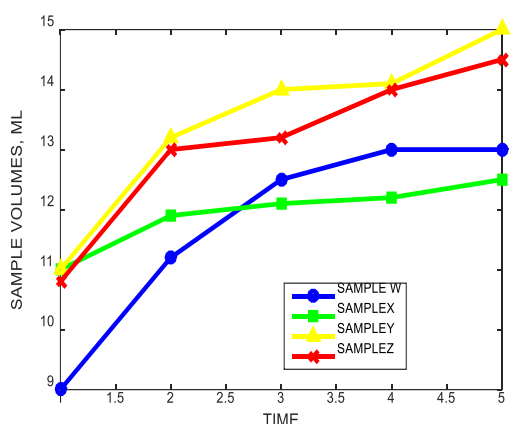


Figure 4: Water Volume Recovered from each Sample for (AGBD1-013L) Emulsion (SLS and Toluene Volumes kept constant)

The result has proven that addition of surfactants and demulsifiers to a crude oil emulsion fosters the treatment of the emulsion by causing a phase separation of the crude and water phases. The major purpose of the surfactant is to modify the interfacial tension between the oil and water phases while the demulsifiers is an additive that mitigates and alleviates the formation of emulsions. The emulsion stability was monitored by measuring the volume of separated water from the emulsion by the test bottle method. Indeed, the lower the emulsion stability, the larger the water partition. The amount of separated water is directly correlated to the instability of the emulsion since destruction of the interfacial film and subsequent water droplet coalescence is the determinant step in the demulsification process. From the

analysis of amounts of separated water for different volume concentrations of hexane (demulsifier) and surfactants, it is noticed that the maximum stability is observed for the emulsion containing the anionic surfactant, whereas the ionic surfactants confer lesser stability to the emulsion.

• Effect of Surfactant on Crude Oil Physical Properties

Since crude oil physical properties is very integral to emulsion formation and its treatment, a comparative analysis is presented in Tables (5-9). The crude oil density, viscosity, cloud point, pour point and pH values are tested under two test scenarios- crude oil with no surfactant and crude oil + surfactant. From the result of the physical properties before addition and after addition of surfactant it shows that there is decrease in density after the addition of surfactant for AGBD1-013L from 0.93g-0.85g and IMOR3-023LS from 0.95g-0.90g. The viscosity of the crude also decreased significantly at the addition of surfactant, for AGBD1-013L from (8.71-5.81)cm/s² while for IMOR3-013L it decreased from (31.61-24.30)cm/s². The cloudpoint of the crude increased for AGBD1-013L from (-2°C to 10.2°C) and for IMOR3-023L from (-1 to 10)°C. The pourpoint increased for AGBD1-013L from (-5 to -2)°C and for IMOR3-023L from (-9 to -1.3)°C. Also a significant increase in PH value for the two crude samples was noted on addition of surfactant. Hence the addition of surfactant in a crude oil caused a significant change in the physical properties of the crude. Details of the calculation are presented in Appendix B.

Table 5: Density of Sample

Sample	Wt of Empty pycnometer (g)	Wt of Pycnometer + crude oil sample (g)	B-A (Wt of Crude Oil Sample) (g)	Density (g/ml)
AGBBI – 013L	14.68	37.93	23.25	0.93
IMOR3 – 023L	14.68	38.55	23.87	0.95
AGBB1-013L+ SLB	14.68	35.95	21.27	0.85
IMOR3-023L+ SLB	14.68	37.20	22.52	0.90

Table 6: Oil Viscosity Measured at a Temperature of 28°C

SAMPLES	Time of Flow (secs)	
	SAMPLE (No Surfactant)	SAMPLE + Surfactant
AGBDI 013L	0.48	40
IMOR3 023L	2.10	1.41



Table 7: Cloud Point of Sample

SAMPLE	CLOUD POINT (°C)	
	SAMPLE (No Surfactant)	SAMPLE + Surfactant
AGBDI-013L	-2	10.2
IMOR3-023L	-1	10

Table 8: Pour Point of Sample

SAMPLE	POUR POINT (°C)	
	SAMPLE (No Surfactant)	SAMPLE + Surfactant
AGBDI-013L	-5	-2
IMOR3-023L	-9	-1.3

Table 9: pH Values @ Average Temperature of 26.0°C

SAMPLE	CLOUD POINT (°C)	
	SAMPLE (No Surfactant)	SAMPLE + Surfactant
AGBDI-013L	6.53	7.41
IMOR3-023L	5.39	7.53

III. CONCLUSION

In this study, the effects of SLS and hexane on crude oil emulsion treatment have been investigated using two different crude oil samples - AGBDI-013L and IMOR3-023L. The samples subjected to similar laboratory conditions and the results are comparatively and collectively analyzed. The result shows that surfactants and demulsifiers greatly affect the physical properties of crude oil by lowering the interfacial tension. Surfactants also lower crude oil density and viscosity and increases the cloud point, pour point and the pH Value. By formulating different emulsion samples, the results reveals that the extent of the effect of surfactants and demulsifiers will be dependent on the type of emulsion to be treated.

In this study, hexane and SLS were added simultaneously and the emulsion stability was measured. For future studies, these substances could be added separately while the stability is measured for each volume concentration.

APPENDIX A EMULSION PREPARATION

The emulsion composed of the crude oil sample, the water, Toluene (stabilizer), SLS (surfactant), and hexane (demulsifier). The total volume of each emulsion sample was equal to 50ml.

Table 10: AGBDI – 013L Emulsion (Hexane and Toluene Volumes kept constant)

Crude Oil Samples			
AGBDI – 013L			
SAMPLE A		SAMPLE B	
Oil	20 ml	Oil	20 ml
Water	15 ml	Water	14 ml
Toluene	4 ml	Toluene	4 ml
SLS	1ml	SLS	2ml
Hexane	10ml	Hexane	10ml
SAMPLE C		SAMPLE D	
Oil	20 ml	Oil	20 ml
Water	13 ml	Water	12 ml
Toluene	4 ml	Toluene	4 ml
SLS	3ml	SLS	4ml
Hexane	10ml	Hexane	10ml

Table 11: IMOR3 – 023L Emulsion (SLS and Toluene Volumes kept constant)

Crude Oil Samples			
IMOR3 – 023L			
SAMPLE E		SAMPLE F	
Oil	20 ml	Oil	20 ml
Water	20 ml	Water	16 ml
Toluene	4 ml	Toluene	4 ml
SLS	1ml	SLS	1ml
Hexane	5ml	Hexane	9ml
SAMPLE G		SAMPLE H	
Oil	20 ml	Oil	20 ml
Water	17 ml	Water	18 ml
Toluene	4 ml	Toluene	4 ml
SLS	1ml	SLS	1ml
Hexane	8ml	Hexane	7ml

Table 12: IMOR3 – 023L Emulsion (Hexane and Toluene Volumes kept constant)

Crude Oil Samples			
IMOR3 – 023L (Toluene and Hexane Constant)			
SAMPLE I		SAMPLE J	
Oil	20 ml	Oil	20 ml
Water	15 ml	Water	16 ml
Toluene	4 ml	Toluene	4 ml
SLS	1ml	SLS	3ml
Hexane	10ml	Hexane	10ml
SAMPLE K		SAMPLE L	
Oil	20 ml	Oil	20 ml
Water	14 ml	Water	12 ml
Toluene	4 ml	Toluene	4 ml
SLS	2ml	SLS	4ml
Hexane	10ml	Hexane	10ml



Table 13: AGBBI – 013L (Toluene and SLS Constant)

Crude Oil Samples			
AGBDI – 013L			
SAMPLE W		SAMPLE Y	
Oil	20 ml	Oil	20 ml
Water	20 ml	Water	17 ml
Toluene	4 ml	Toluene	4 ml
SLS	1ml	SLS	1ml
Hexane	5ml	Hexane	8ml
SAMPLE X		SAMPLE Z	
Oil	20 ml	Oil	20 ml
Water	15 ml	Water	18 ml
Toluene	4 ml	Toluene	4 ml
SLS	1ml	SLS	1ml
Hexane	10ml	Hexane	7ml

APPENDIX B

EXPERIMENTAL CALCULATIONS

a. Density

Weight of empty pycnometer = 14.48 + 0.25 = 14.68g

AGBDI-013L

Weight of pycnometer + crude oil = 37.68 + 0.25 = 37.93g

Weight of crude oil = **23.25g**

IMOR3-023L

Weight of pycnometer + crude oil = 38.30 + 0.25 = 38.55g

Weight of crude oil = **23.87g**

$$\text{Specific gravity, } \rho = \frac{\rho_o \left(\frac{g}{ml} \right)}{\rho_w \left(\frac{g}{ml} \right)}$$

$$\text{But, Density} = \frac{\text{mass}}{\text{volume}}$$

$$API = \frac{141.5}{SG} - 131.5$$

$$AGBBI - 013L : \text{Density} = \frac{23.25}{25} = 0.93 \text{ g/ml}$$

$$IMOR3 - 023L : \text{Density} = \frac{23.87}{25} = 0.95 \text{ g/ml}$$

Density of water = 1 g/ml

Specific gravity of AGBDI-013L

$$\text{Specific gravity} = \frac{0.93 \left(\frac{g}{ml} \right)}{1 \left(\frac{g}{ml} \right)} = 0.93$$

Specific gravity of IMOR-023L

$$\text{Specific gravity} = \frac{0.95 \left(\frac{g}{ml} \right)}{1 \left(\frac{g}{ml} \right)} = 0.95$$

$$API \text{ of AGBDI} - 013L = \frac{141.5}{0.93} - 131.5 = \mathbf{20.65^{\circ}A}$$

$$API \text{ of IMOR} - 023L = \frac{141.5}{0.95} - 131.5 = \mathbf{17.45^{\circ}A}$$

b. Oil Viscosity

Using the formula:

$$\left(At - \frac{B}{t} \right) cm/s^2$$

Where;

$$A = 0.264, B = 190 \quad \text{for } 40 \text{ s} < t < 85 \text{ s}$$

$$A = 0.247, B = 65 \quad \text{for } 85 \text{ s} < t < 2000 \text{ s}$$

$$AGBDI - 013 \text{ L (Viscosity)} \quad [t = 48 \text{ sec}]$$

$$\left(0.264 \times 48 - \frac{190}{48} \right) = \mathbf{8.71 cm/s^2}$$

$$IMOR3 - 013 \text{ L (Viscosity)} \quad [t = 130 \text{ sec}]$$

$$\left(0.247 \times 130 - \frac{65}{130} \right) = \mathbf{31.61 cm/s^2}$$

Results on Addition of Surfactant

a. Density

Weight of empty pycnometer = 14.48 + 0.25 = 14.68g

AGBDI-013L

Weight of pycnometer + crude oil = 35.70 + 0.25 = 35.95g

Weight of crude oil = **21.27g**

IMOR3-023L

Weight of pycnometer + crude oil = 36.95 + 0.25 = 37.20g

Weight of crude oil = **22.52g**

$$\text{Specific gravity, } \rho = \frac{\rho_o \left(\frac{g}{ml} \right)}{\rho_w \left(\frac{g}{ml} \right)}$$

$$\text{But, Density} = \frac{\text{mass}}{\text{volume}}$$

$$API = \frac{141.5}{SG} - 131.5$$

Volume of pycnometer = 25 ml

$$AGBDI - 013L : \text{Density} = \frac{21.27}{25} = \mathbf{0.85 g/ml}$$

$$IMOR3 - 023L : \text{Density} = \frac{22.52}{25} = \mathbf{0.90 g/ml}$$

Density of water = 1 g/ml

Specific gravity of AGBDI-013L

$$\text{Specific gravity} = \frac{0.85 \left(\frac{g}{ml} \right)}{1 \left(\frac{g}{ml} \right)} = 0.85$$

Specific gravity of IMOR-023L

$$\text{Specific gravity} = \frac{0.90 \left(\frac{g}{ml} \right)}{1 \left(\frac{g}{ml} \right)} = 0.90$$



$$API \text{ of AGBDI} - 013L = \frac{141.5}{0.85} - 131.5 = \mathbf{34.97^0 AP1}$$

$$API \text{ of IMOR} - 023L = \frac{141.5}{0.90} - 131.5 = \mathbf{25.72^0 AP1}$$

b. Viscosity

Using the formula:

$$\left(At - \frac{B}{t} \right) cm/s^2$$

Where;

$$A = 0.264, B = 190 \quad \text{for } 40 \text{ s} < t < 85 \text{ s}$$

$$A = 0.247, B = 65 \quad \text{for } 85 \text{ s} < t < 2000 \text{ s}$$

AGBDI- O13 L (Viscosity) [t = 40 sec]

$$\left(0.264 \times 40 - \frac{190}{40} \right) = \mathbf{5.81 cm/s^2}$$

IMOR3 - O13 L (Viscosity)[t = 101 sec]

$$\left(0.247 \times 101 - \frac{65}{101} \right) = \mathbf{24.30 cm/s^2}$$

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