academicJournals

Vol. 4(8), pp. 198-202, December, 2013
DOI: 10.5897/JPGE2013.0177
ISSN 2141-2677 ©2013 Academic Journals
http://www.academicjournals.org/JPGE

Journal of Petroleum and Gas Engineering

Full Length Research Paper

Effect of pH on interfacial tension and crude oil–water emulsion resolution in the Niger Delta

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Accepted 19 December, 2013

It is important to know the produced volumes and to effectively separate the oil and water phases in oil well effluents to the surface during production. While it is known that the effectiveness of separating the phases and hence the accuracy of measurements are often affected by the nature of the fluids, the specific contributions of the physical parameters of the fluids are little known. In this study, the effect of crude oil PH on emulsion resolution was investigated. Crude oil samples from the Niger Delta with known amounts of water present were obtained. After obtaining the pH and interfacial tension, the oil and water phases were separated by centrifuge at different speeds. The results were used to establish a relationship between interfacial tension, pH and the basic sediments and water (BSW). The results show that without the use of de-emulsifiers, separation of between 66 and 90% was achieved in the light crude oil samples, but less than 30% in heavy crudes. Oil pH was found to affect emulsion resolution and has implications on the choice of de-emulsifiers. On the other hand, interfacial tension was independent of the volume of water and hence BSW of the crude oil samples.

Key words: Oil production, interfacial tension, basic sediments and water (BSW), Niger Delta, bottle test.

INTRODUCTION

Most oil wells produce petroleum with some basic sediments and water. High flow rates and agitation along the production tubings and flow lines could lead to formation of emulsions. Interfacial tension is created at the oil-water interface as a result of imbalance of molecular forces of the dissimilar molecules (McCain Jnr, 1990). Interfacial tension is an indication of the degree of surface activity of a given crude-brine system (McCaffery, 1972) and it is a function of the dispersion forces of the oil and water molecules (Fowkes, 1964). Interfacial tension has been defined as the work required creating a unit area of interface at a constant temperature, pressure, and chemical potential (Drelich et al., 2002; Abhijit, 2006). According to Gong et al. (2001), interfacial tension can be static or dynamic. Static interfacial tension measures the excess energy associated with unsaturated inter-molecular interactions which tend to drive the interface to adopt geometries that minimize the interfacial area while dynamic interfacial tension measures freshly created interfaces (Buckley and Tianguang, 2005).

Over the years, several methods have been employed in the measurement of interfacial tension. These have been classified as direct and indirect measurement methods (Drelich et al., 2002). Direct measurement involves the use of Wilhemy plate or the du Nuoy ring to measure the excess energy per unit length either by static measurement or in detachment mode (Isehunwa and Olanisebe, 2012).

A wide range of methods have been used to measure the BSW of crude oil during production. (EESFLOW, 2007). Warren (1962) developed a technique of measuring BSW using dielectric-constant. It works on the basis of variation of impedance and circuit phase angle with cell capacitance which changes when cell is filled with clean oil and increases when filled with wet oil. The sensitivity to other contaminants other than water and

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influence of viscosity at lower temperatures on the dielectric constant are major issues of Warren's technique despite its widespread use.

The installation of water-cut meters which measures oil and water production at time intervals is another widely used method. The meter measures the properties of the production fluids which is mainly oil and water and analyses the differences in their properties translating the results to volumetric concentrations. The major disadvantages of this method are its expensive installation process, inefficiency at elevated temperatures, unsuitability for saline crudes and incorrect field calibration. Manual estimation of BSW has also been done by the grab sample analysis and the well known bottle test method. The bottle test method is laborious in that it involves visual observation of phase separation, difficult task of efficient demulsifier selection, time consuming and costly. Furthermore, data obtained from this method could be unreliable because samples used are often taken in batches and may not be representative of the total flow line and makes data reconciliation a necessity.

Obtaining accurate estimates of oil and water produced in simple and cost effective ways over a wide range of operational conditions is a continued challenge to the oil petroleum industry and has led to studies on measurement of BSW based on parameters such as critical electric field and or the interfacial tension of crude oil-water systems. This work investigated the relationship between BSW, pH and interfacial tension of crude oil systems.

THEORETICAL FRAMEWORK

The relationship between capillary pressure and centrifuge data has been noted by several researchers such as Slobod (1951), Bentsen (1977), Melrose (1988) and Abhijit (2006). It should be possible to extend the relationship to interfacial tension and BS&W.

In general, the pressure difference between two immiscible fluids is given by:

$$\Delta P = (\rho_1 - \rho_2) g h \quad (1)$$

Using the method of Hassler and Brunner (1945), the relation between capillary pressure and average saturation of cores in centrifugal field can be written as:

$$P_{c,r_1} = \frac{1}{2} \Delta\rho\, \omega^2 (r_2^2 - r_1^2) \quad (2)$$

Using Equation (2):

$$r = r_2 \sqrt{1 - \frac{P_c}{\frac{1}{2}\Delta\rho w^2 r_2^2}} \quad (3)$$

$$a = \frac{v^2}{r} \quad (4)$$

$$v = \frac{2\pi r w}{60} \quad (5)$$

$$a = \frac{4\pi^2 r w^2}{3600}$$

Acceleration due to gravity g in Equation (1) is converted to centrifugal gravity g' by dividing centrifugal acceleration by acceleration due to gravity g;

$$g' = \frac{4\pi^2 r w^2}{3600\, g} = 0.00001119\, r\, w^2 \quad (7)$$

Using Slobod et al. (1951) relations for acceleration in the centrifuge [Equations (4) to (7)], Equation (1) can be expressed as:

$$\Delta P = (\rho_1 - \rho_2)\, g'\, h \quad (\frac{g}{cm^2})$$

Substituting values and converting $(\frac{g}{cm^2})$ to psig, Equation (8) becomes:

$$\Delta P = 1.5912 * 10^{-7}\ (\rho_1 - \rho_2)\, w^2\, r\, h$$

Given that

$$h = r_2 - r_1 \; and \; r = \frac{r_2 + r_1}{2}$$

and assuming capillary pressure at the outer face of the centrifuge tube is zero, then for a centrifuge with r_1 and r_2 of 5.0 and 5.7 cm respectively, the capillary pressure at any particular rpm can be expressed as:

$$P_c(r) = 7.956 * 10^{-8} (\rho_1 - \rho_2)\, w^2\, (r_2^2 - r_1^2)$$

Or, in general:

$$P_c(r) = Y * w^2\, Psig \quad (11)$$

Where, Y is a constant that varies with the centrifuge speed, and crude oil type. From the well-known relationship between capillary pressure and interfacial tension of two immiscible fluids, the interfacial tension can be expressed as:

$$\sigma_{ow} = \frac{P_c(r)}{2(Cos\ \theta)} \quad (12)$$

Where,

Table 1. Average properties of crude oil samples.

Crude oil	Density (g/cm^3)	pH	API	Static interfacial tension (dynes/cm)	Y (Equation 11)
Sample A	0.82	6.5	40	11.8	4.32×10^4
Sample B	0.83	5.2	56	8.4	10.0×10^4
Sample C	0.88	6.2	29	8.4	7.17×10^4
Sample D	0.87	7.3	32	13.5	8.60×10^4
Sample E	0.93	7.8	21	22.8	2.18×10^4

$$\cos\theta = \frac{r_1}{r_2} \quad (13)$$

Thus, combining Equations (11) to (13), dynamic interfacial tension can be determined.

MATERIALS AND METHODS

Crude oil samples obtained from five different reservoirs were collected and emulsified by rigorous mixing with known quantities of water. pH was measured using an analytical pH meter while interfacial tension was measured using the CSC-DuNouy Tensiometer. The Hermle Centrifuge model Z323 was used to separate the water and crude at 2000, 3000 and 4000 rpm over a duration of 5 min. Results were analyzed by adapting the derivations of Hassler and Brunner (1945).

RESULTS AND DISCUSSION

The crude oil samples used varied from light to heavy crudes; with density ranging from 0.82 to 0.93 g/cc. Detailed average physical properties of the samples at room temperature of 29°C are presented in Table 1. Table 2 shows the estimated dynamic interfacial tension using Equations (10) to (13).

Table 3 shows that the percentage of water recovered from the oil centrifuged at 4000 rpm varied with the initial BSW for each crude oil sample. The recovery of samples A, B and C increased with increasing initial percentage BSW giving an average of 70% recovery while samples D and E gave an average recovery of 20%. This shows that crude oil samples D and E did not readily separate at higher water content and centrifugal revolution per minute. The incomplete recovery of water in the water-in-oil emulsions in all the crude oil samples shows that full resolution cannot be achieved by only centrifugation without use of de-emulsifiers.

Furthermore, it was observed that the static interfacial tension values obtained by the Du Nouy Ring method in Table 1 were quite different from the calculated dynamic interfacial tension using capillary pressure and shown in Figures 3 and 4. This is as a result of continuous structural changes which occur on both sides of the physical interface of the two fluids in contact. According to Drelich et al. (2002), the creation of fresh surfaces is accompanied by constantly refreshed surfaces of which composition has not reached equilibrium. The dynamic interfacial tension at these interfaces is therefore low because solute redistribution has not yet occurred between the water and crude oil phases. The process of agitation while using the centrifuge continuously creates fresh interface in the crude oil-water system.

Figures 3 and 4 show that the behavior of dynamic interfacial tension and BSW at different revolution per minute of centrifuge. The plots show that while interfacial tension increases with the rpm of the centrifuge, the interfacial tension does not vary with BSW. This result is perhaps due to the fact that since interfacial tension involves adhesive forces between the two liquid phases, interaction occurs at the interface of the fluids involved and does not therefore depend on the relative amounts of the immiscible fluids present. The practical implication of this is that BSW may not be accurately determined from the measurement of interfacial tension.

Furthermore, it was observed that pH has a strong effect on the Interfacial tension and on the volume of water recovered after centrifuge. The relationships were established by Equations (14) and (15) as:

$$y = 3.0553x^2 - 34.722x + 106.8 \quad (14)$$

While,

$$P = 26.254x^2 - 313.91x + 957.13 \quad (15)$$

Where, $y = static\ interfacial\ tension,$ and $P = BSW\ (\%)\ (after\ \text{centrifuge})$, and $x = \text{pH}\ (5.2 < x < 7.6)$

The coefficients of correlation (R^2) were estimated as 0.92 and 0.96 for Equations (14) and (15) respectively (Figures 1 and 2).

Conclusion

This study revealed the following:

1. Interfacial tension is an interface phenomenon and is not affected by the volume of water present in crude. The practical implication is that in an oil-water system, interfacial

Table 2. Dynamic Interfacial tension of emulsified crude samples during centrifuge.

Rotary speed (rpm)	Interfacial Tension (dynes/cm)				
	A	B	C	D	E
2000	0.56	1.34	0.93	1.12	0.28
3000	1.26	2.93	2.09	2.52	0.64
4000	2.24	5.21	3.73	4.47	1.13

Table 3. Percentage water recovery.

Initial BSW (%)	% Water recovered after centrifuge at 4000 rpm				
	A	B	C	D	E
9.1	77	83	88	12	33
16.7	51	78	90	24	24
23.1	69	65	91	12	20
28.6	67	64	88	14.7	18
19.4*	66.0*	72.5*	89.3*	18.2*	23.8*

*Average.

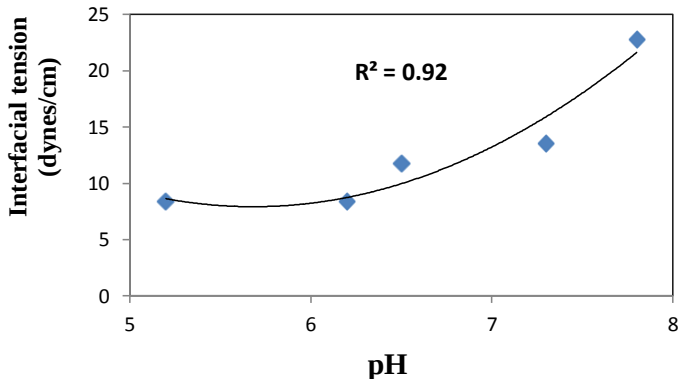

Figure 1. Interfacial tension (dynes/cm) versus pH.

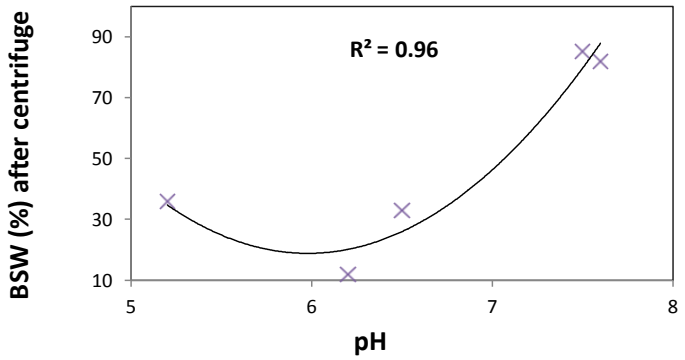

Figure 2. BSW (%) after centrifuging against pH.

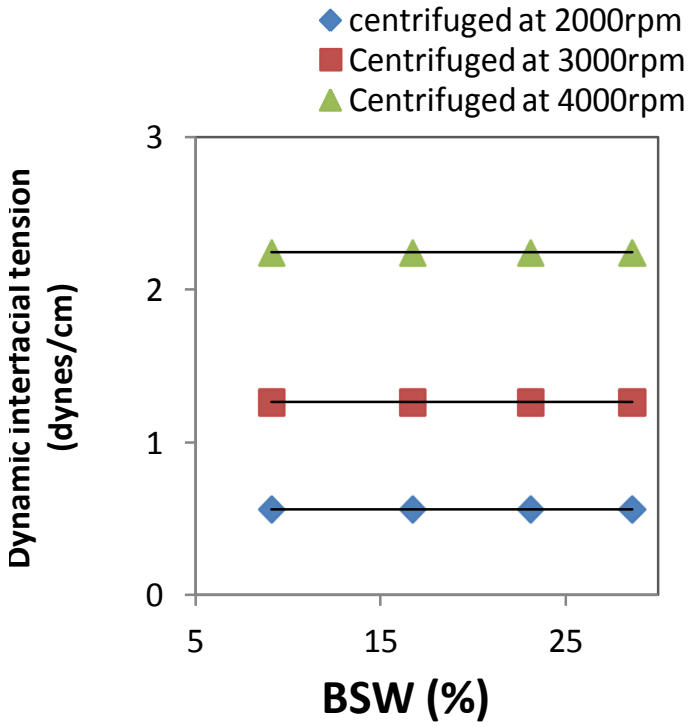

Figure 3. Interfacial tension (dynes/cm) versus (dynes/cm) versus BSW (%) of sample A at different rpm.

tension may not be a good correlator of the relative volumes of the fluids present.

2. pH of crude samples affect the volume of water recovered and also affects interfacial tension. This observation has implications on the choice of de-emulsifiers and their effectiveness in breaking oil-water emulsions.

3. Static interfacial tension of crude oil-water system is higher than dynamic interfacial tension.

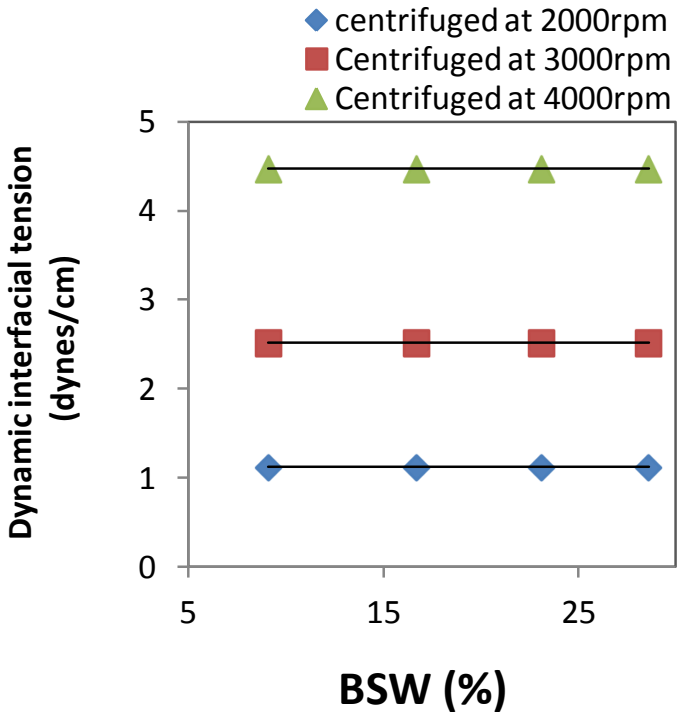

Figure 4. Interfacial tension BSW (%) of sample D at different rpm.

ACKNOWLEDGMENT

This study was supported through research grant from the Shell Petroleum Development Company to the Shell Professorial Chair in Petroleum Engineering, University of Ibadan.

Nomenclature: ΔP, Pressure difference (psia); h, height above the reference level (cm); ρ_1, ρ_2, densities of the two fluids present (g/cc); g, acceleration due to gravity (cm/s^2); w, centrifuge angular speed (rpm); σ_{ow}, oil-water interfacial tension; θ, contact angle; **Pc,** capillary pressure, psig; **Y,** constant that depends on centrifuge speed.

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