

Effect of Temperature and Contamination on the Surface Tension of Niger Delta Crude Oils

¹Isehunwa, S.O., ²Udeagbara, S.G. and ³Akpabio, J.U.

^{1,2,3}Department of Petroleum Engineering University of Ibadan, Nigeria.

Abstract: Surface tension is an important property that affects the behavior and characteristics of reservoir fluids. It impacts the capillary pressure and fluid dynamics in porous media. This study, investigated the surface tension of Contaminated Niger Delta crude oil at varying temperatures. Laboratory tests were carried out on samples from four fields in the Niger Delta using DuNouy Tensiometer under standard conditions. The results show that for Niger Delta Crudes of gravity between 25 - 49 API, Surface Tension varies between 25.8 - 31.2 dynes/cm at 29°C and decreases to between 21.5-26.6 dynes/cm at 90°C. Surface Tension of the crudes was also affected by salt contamination, bentonite and mud filtrate and surfactant contamination. Contamination by bentonite also increased the surface tension from about 28 to 34 dynes/cm. predictive models have been developed as a quick-look tool for estimating surface tension of Niger Delta crude oil and similar reservoir fluids.

Key words: Niger Delta, Surface Tension, Temperature, Contamination, Crude oil.

INTRODUCTION

Surface tension is a cohesive quality of liquids that gives their surfaces a slightly elastic quality and enables them to form into separate drops. It is caused by the interaction of molecules at or near the surface that tend to cohere and contract the surface into the smallest possible area. It depends on the nature of the liquid, the surrounding environment and temperature. Surface tension results from an imbalance of molecular forces in a liquid. At the surface of the liquid, the molecules are attracted to each other and exert a net force pulling them together.

Surface tension is useful in estimating capillary pressure forces in porous media and is an input parameter in some correlations used in well bore hydraulics calculations. It is also used in predicting the effects of some substances used in completion operations as well as in multiphase pipe flow, gas/liquid and liquid/liquid processes to determine the flow patterns and liquid holdup. Surface tension is not a property of the liquid alone, but of the liquid's interface with another medium. In general, surface tension decreases with increase in temperature as cohesive forces decrease with an increase of molecular thermal activity. The influence of the surrounding environment is due to the adhesive action liquid molecules have on the interface.

Experimental methods of determining surface tension can be classified into two methods: Static and Dynamic methods. The static methods include: Capillary rise, Sessile drop, Pendant drop, Drop Weight (slow), Maximum bubble pressure and Wilhelmy plate methods. Dynamic methods are: Capillary waves, Unstable jets, DuNouy ring (rapid), Drop weight (fast), Wilhelmy plate and Spinning drop methods. The objective of this work was to determine the effect of temperature on the surface tension of contaminated Niger Delta Crude.

The surface tension of aqueous solutions is of interest for several reasons. From a scientific point of view, it gives information on the structures and energies at the air-liquid interface. The surface tension of aqueous solutions plays a key role in the flow of various fluids in porous media. It is also important in studies related to understanding structures of molecules at the interface, mass transfer processes, enhanced oil recovery, using gas injection, and flow of contaminants in soils. The surface tension of some additives (e.g. brine and bentonite) used in completion operation play a key role in determining the productivity of gas wells. A low surface tension is required to reduce the capillary forces that trap the aqueous phase in the formation. Accumulation of the aqueous phase near the well bore area, known as water blockage, leads to a reduction in the relative permeability of gas, which can in turn, significantly reduce well productivity

Ramsay and Shields (1893) draw attention to a certain resemblance between the alteration of surface tension with temperature and the alteration of gaseous pressure with temperature. They pointed out that the surface tension increases linearly as the temperature falls below a certain temperature, while the gaseous pressure increases linearly as the temperature rises from absolute zero.

Corresponding Author: Isehunwa, S.O., Department of Petroleum Engineering University of Ibadan, Nigeria.

Neil, (1938) pointed out that surface tension, as the free energy per unit area, is the work done in dragging molecules required to form the fresh surface from the interior to the surface against the inward pull of the molecules underlying the surface, which is exerted on the surface molecules. It is therefore a measure of the intensity of this inward pull. In his work, he pointed out that the kinetic agitation of the molecules and the tendency of the molecules to fly outwards increases as the temperature rises.

Nasr-EL-Din, *et al.* (2004) established a relationship between surface tension and temperature. His results show that surface tension decrease linearly with temperature. Adduraham and Rosli (2006) investigated the influence of salt concentration, mixing speed, water concentration, as well as temperature on emulsion stability. Their findings showed that there is a strong relationship between these parameters and emulsion stability.

MATERIAL AND METHODS

Samples of crude oil were obtained from four fields in the Niger Delta and characterized for physical properties. The DuNouy Tensiometer was then used to measure Surface tension of the fluids. Crude oil samples were heated in a water bath at temperatures between 30 - 90°C and measurements were taken at 10°C intervals. The experiments were conducted using standard procedures. The effect of bentonite on the surface tension of the four crude oils was also estimated using different concentrations of bentonite between 0.012 – 0.101ppm. The effect of salinity on the surface tension of the crude oils was also estimated using different concentrations of Sodium Chloride (NaCl) between 0.022 – 0.109ppm. The effect of surface tension of water-in-oil emulsion was determined from prepared samples (mixture of water and crude oil) using 10 – 40ml of water and four measurements taken for the different crude types at intervals of 10ml.

RESULTS AND DISCUSSION

The Physicochemical properties of the crude oils used are shown in Table 1 which show that the Density of the crudes varies from 0.77-0.89 g/cm³, the API gravity is between 25-49.2 and the viscosity is between 1.0-18cp and specific gravity is between 0.77 - 0.90.

The measurements taken in each of the experiments were corrected to the real values using a correction factor obtained from Equation 2. This correction factor offsets properties of both ring and sample at the point of detachment. The actual surface tension is given as:

$$A = P * F \tag{1}$$

Where

A = actual surface tension

P = Apparent Surface Tension (dial reading)

F = correction factor

Correction factor (F) can be determined with the following formula:

$$F = 0.7250 + \sqrt{\frac{0.01452P}{C^2(D-d)} + 0.04534} - \frac{1.679r}{R} \tag{2}$$

Where

F = correction factor

P = Dial reading

C = Ring circumference

D = Density of lower phase

d = Density of upper phase

R = Radius of ring

r = Radius of the ring wire

Surface tension obtained in this work agreed with Bikerman (1958) who noted that the surface tension of petroleum fluids is expected to vary between 20 and 38 dynes/cm at room temperature.

However, the surface tension was measured for different temperature values in the experiment and its value for the four samples varies linearly from 30-90°C. Table 2 shows the effect of Temperature on surface tension of Crude oil and water as the base case. Table 3 shows the effect of salinity on Surface tension of Crude oil and Table 4 shows the effect of bentonite concentration on the surface tension of crude oil.

Effect of Temperature on Contaminated Crude Oils:

It can be deduced that continuous heating of the crude oil will keep on reducing the surface tension until you get to critical temperature where surface tension ceases to exist. At this point the crude oil no longer exist as liquid but rather as vapour as shown in Figure 1 which indicates that there is a fairly good linear relationship between surface tension and temperature. It shows that the higher the temperature the lower the surface tension for the four crudes A, B, C and D. The high R² values of 0.86378, 0.86089, 0.85791 and 0.86095 for crude oils A, B, C and D respectively show that 86.37%, 86.08%, 85.79% and 86.09% of the variation in surface tension of the four crude oils are accounted for by the independent variable (temperature).

These high R² values show that there is a strong relationship between surface tension and temperature (the dependent and independent variable) in the absence of any additive that may interfere with the effect of temperature on surface tensions of the crude oil properties. Crude oil A gives higher value of surface tension than the other crudes; it has properties different from crude oil B, C and D. Table 1 show that it is heavy oil with high viscosity and low API gravity (25.03). Crude oil B and D share similar properties, they have almost the same surface tension values with temperature, they are light oils with low viscosity values and high API gravities of 45.20 and 44.86 respectively. Crude oil C has the least value of surface tension with temperature; it is the lightest oil with the lowest viscosity value and the highest API gravity (49.26).

From the Figures 1-5, equations were also generated for the prediction of surface tension of the crude oils at a particular temperature. The equations are called prediction equations and they are generally represented in this form for each crude oil sample:

$$Y = \alpha X + \beta \tag{3}$$

Where α = the slope, dynes/cm/°C

β = the Y-intercept at room temperature, dynes/cm

Y = surface tension, dynes/cm

X = temperature, °C

α = -0.0749, -0.0708, -0.0697 and -0.0668 for crude oils A, B, C and D respectively while β = 31.23, 26.84, 26.10 and 25.65 for crude oils A, B, C and D respectively. Figure 2 shows the correlation between API gravity and surface tension at a constant temperature. Crude oil A with the lowest API value has the highest surface tension but the reverse is the case for crude B, C and D. With a temperature difference of 40°C the surface tension reduces by about 3 dynes/cm Figure 3 shows that the higher the viscosity, the higher the surface tension and the heavier the oil. With a temperature difference of 40°C the surface tension reduces by about 3 dynes/cm. It therefore means that to produce such oil, the temperature has to be so high that it makes the oil lighter and easier to escape to the surface. From the analysis of the oil samples, it can be deduced that the higher the viscosity, the lower the °API and the thicker the oil; consequently, the lower the viscosity the higher the °API and the lighter the oil.

Figures 4 show the plot of surface tension against some parameters associated with crude oils containing brine (sodium chloride). It is a plot of surface tension of crude oil A, B and C against the concentration of salt which shows a linear relationship and reveals that the higher the concentration of salt the higher the surface tension i.e. the dependent variable (surface tension) is actually being controlled by the independent variable (concentration of salt). It also shows that crude A has the highest value of surface tension followed by crude B and C in that order. Here the coefficient of determination (r²) as calculated from the plot is 0.8428, 0.8259 and 0.8259 for A, B and C respectively. This high value of r² indicates that there is a strong positive relationship between the dependent and independent variables. It can be deduced from the plot that the heavier the oil, the more the viscosity, the higher the surface tension. The prediction equations for the three crude oils A, B and C are also expressed as Equation 3 where α is slope and equal 0.391, 0.104 and 0.104 for A, B and C while β is intercept at 0.022 ppm and equal 31.58, 28.74 and 28.68 for A, B and C respectively.

The equations for the prediction of surface tension of the crude oils at any given mass of bentonite is expressed as Equation 3 where α = 0.2331, 0.2939, 0.2215 and 0.1922 and β is intercept at 1 gram of bentonite equal 32.34, 27.45, 27.15 and 28.02 for Crude oils A, B, C and D respectively.

The same trend is applicable where a higher concentration of bentonite in solution yields a higher value of surface tension.

Figure 5 shows a plot of surface tension against concentration of bentonite. The figure indicates that there is a good linear relationship between the dependent and independent variables (surface tension and concentration of bentonite). For the four crude oil samples used, it was observed that the higher the concentration of bentonite in solution, the higher the surface tension. Impurities can therefore increase or decrease surface tension depending on the type used. From the values of the coefficient of determination calculated (R^2), they show that there exist a strong positive relationship between the dependent and independent variable. It therefore follows that 74.48%, 75.20%, 74.68% and 74.41% of the variation in the surface tension of the crude oil samples A to D respectively are accounted for by the independent variable. It should also be noted that the higher the percentage the stronger the relationship. In this case crude oil B shows a stronger relationship followed by crude oil C, A and D in that order. From the laboratory analysis, crude oil A was found to be highly viscous crude with low API gravity hence heavy oil. Crude B and D exhibit a similar relationship of course their densities, specific gravities and API gravities values are close, though their surface tension values increase with increase in concentration of Bentonite, and they give much lower values when compared with crude A. Both crude B and D are light oil with high API gravity. Crude oil C exhibits the least value of surface tension (though not too far from crude B and D) as the concentration of Bentonite increases. It is the lightest oil with the highest API gravity and the lowest viscosity value.

Emulsion has been a serious problem in oil industry because it has to be broken so that water separates from oil and this makes the production and processing easier. Crude oil A which is a heavy oil with high viscosity and low API gravity gives the highest value of surface tension upon the formation of the emulsion. Crude oil B, C and D also follow the same linear relationship as in crude oil A. Their surface tension values increase as volume of water increases. Crude oil B and D with almost the same API gravity exhibit similar values of surface tension, both are light oil with high API gravity and low viscosity. Crude oil C is the lightest with the lowest value of surface tension upon the formation of emulsion. It can be concluded that the lighter the oil, the lower the surface tension and the easier it is to break the emulsion using a demulsifier like surfactants.

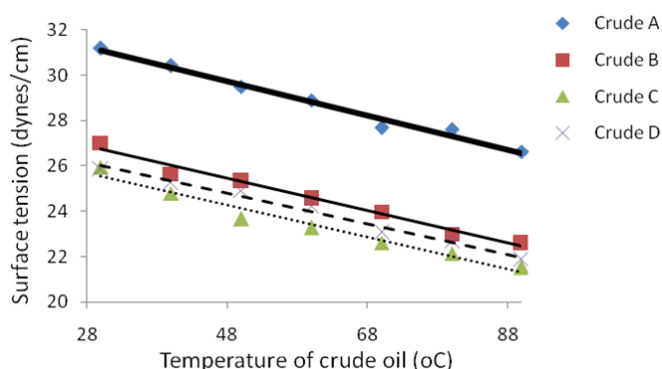


Fig. 1: Surfacetension vs. Temperature of crude oil.

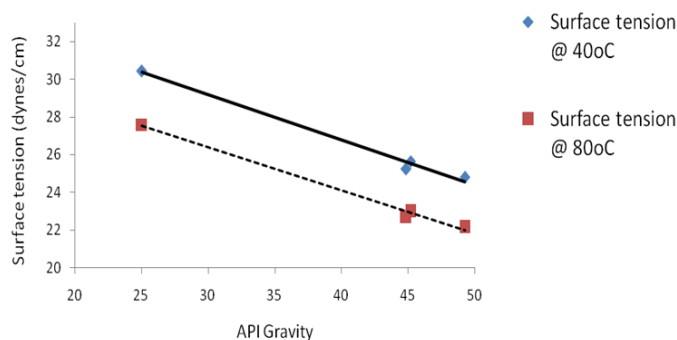


Fig. 2: Surfacetension vs. API gravity of crude oil.

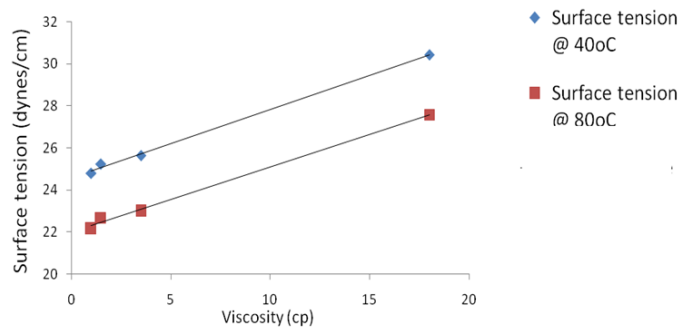


Fig. 3: Surfacetension vs. Viscosity of crude oil.

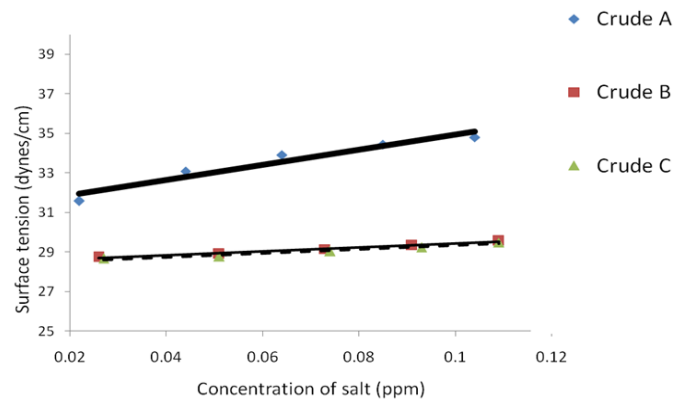


Fig. 4: Surfacetension vs. Concentration of salt in oil sample.

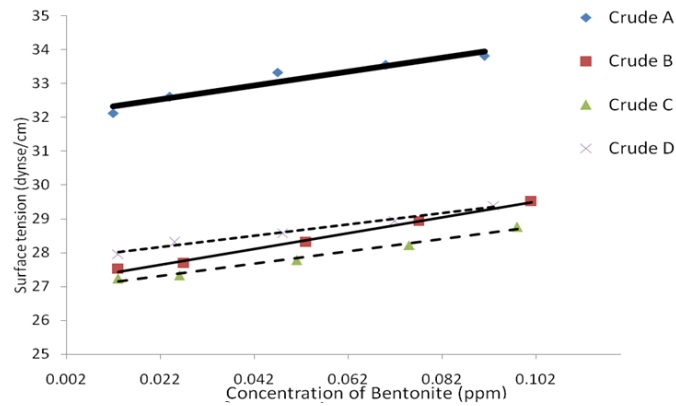


Fig. 5: Surfacetension vs. Concentration of Bentonite in crude oil.

Table 1: Physicochemical properties of the crude oils, A, B, C, and D.

Crude oil Sample	Crude A	Crude B	Crude C	Crude D
Density (g/cm ³)	0.89	0.79	0.77	0.79
Viscosity (cp)	18.00	3.50	1.00	1.50
API	25.03	45.20	49.26	44.86
BS &W	0.1	0.1	0.1	0.05
Specific Gravity	0.90	0.80	0.77	0.80

Table 2: Effect of Temperature on Surface Tension of crude oil and water.

Temperature (oC)	Surface tension (dynes/cm)				
	Crude A	Crude B	Crude C	Crude D	water
30	31.20	27.03	25.96	25.84	71.87
40	30.43	25.65	24.80	25.24	68.17
50	29.50	25.33	23.67	24.92	66.07
60	28.90	24.56	23.27	24.24	64.70
70	27.68	23.98	22.62	23.06	62.69
80	27.59	23.00	22.15	22.68	61.24
90	26.64	22.59	21.51	21.86	59.53

Table 3: Effect of Salinity on Surface Tension of Crude Oil.

Crude A		Crude B		Crude C	
Salinity (ppm)	Surface tension	Salinity (ppm)	Surface tension	Salinity (ppm)	Surface tension
0.022	31.58	0.026	28.74	0.027	28.68
0.044	33.09	0.051	28.91	0.051	28.77
0.064	33.92	0.073	29.15	0.074	29.04
0.085	34.45	0.091	29.33	0.093	29.23
0.104	34.81	0.109	29.57	0.109	29.49

Table 4: Effect of Bentonite on Surface Tension of Crude Oil at room Temperature.

Crude A		Crude B		Crude C		Crude D	
Concentration (ppm)	Surface tension	Concentration (ppm)	Surface tension	Concentration (ppm)	Surface tension	Concentration (ppm)	Surface tension
0.012	32.13	0.013	27.51	0.013	27.23	0.013	27.96
0.024	32.61	0.027	27.68	0.026	27.33	0.025	28.31
0.047	33.33	0.053	28.31	0.051	27.78	0.048	28.58
0.070	33.55	0.077	28.94	0.075	28.22	0.072	28.94
0.091	33.81	0.101	29.51	0.098	28.76	0.093	29.39

Conclusion:

It was observed that increased temperature decreases the surface tension of Niger Delta crude oils while water-in-oil emulsion increases the surface tension. Contamination by salt and bentonite also increase the surface tension of both crude oil and water. The relationship between surface tension and temperature is very strong in crude oil compared with that of water and other additives. Presence of bentonite as contaminant in crude oil decreases the API gravity and increases the viscosity of the oil.

ACKNOWLEDGEMENT

The support of the Laboratory staff in the Department of Petroleum Engineering, University of Ibadan is acknowledged.

REFERENCES

Abdurahman, H.N., M.Y. Rosli, 2006. "Stability of Water-in-Crude Oil Emulsion", *J. Applied Sci.*, 6(14): 2895-2900.

Blair, C.M., 1945. "Oil and Gas Journal", 44: 116-127.

Bikerman, J.J., 1958. "Surface Chemistry, Theory and Application", Academic Press Inc., New York, 1958.

Boyce, J.F., S. Schurch, Y. Rotenberg, A.W. Neumann, 1984. "The measurement of Surface and Interfacial Tension by the Axisymmetric Drop Technique", *Colloids and Surfaces*, 9: 307.

Clark, N.J., 1969. "Elements of Petroleum Reservoir", SPE, Richardson, TX, U.S.A. Manual-CSC Scientific DuNouy Tensiometers.

Collins, R.E., 1990. "Flow of fluid Through Porous Material", Research and Engineering Consultants, Inc., Colorado.

Dabbousi, H.A., Nasr-El-Din, SPE, A.S. Al-Muhaish, 1999. "Influence of Oilfield Chemicals on the Surface Tension of Stimulating Fluids", Paper SPE 50732, Presented at the 1999 SPE International Symposium on Oilfield Chemistry Held in Houston, Texas, February 16-19.

Howard, B.B., W.P. Fred, M. Mohammad, 2003. "Petroleum Engineering Handbook", Society of Petroleum Engineers (SPE), Richardson, TX, U.S.A.

- Harley, Y.J., 1974. "A Study of Solution-Crude Oil Interfacial Tensions", Paper SPE 5049, Chevron Oil Field Research Company, La Habra California.
- Hansen, F.K., G. Rodsrud, 1991. "Surface Tension by Pendant Drop", *J. Colloid Interface Sci.*, 141(1): 1.
- Harkins, W.D: "The Physical Chemistry of Surface Films", Reinhold, New York, 1952.
- Jamal, S., 2002. "Fluid Flow Handbook", Mc Graw-Hill Companies, Inc.
- Kenneth, J.L., 1984. "Emulsions and Emulsion Technology: Part 111", Marcel Dekker, Inc., New York.
- Katz, D.I., R.R. Monroe, R.P. Trainer, 1943. "Surface Tension of Crude oils containing Dissolved Gases", *JPT* pp: 21.
- Neil, K.A., 1938. "The Physics and Chemistry of the Surfaces", Second Edition, The Clarendon Press.
- Nasr-El-Din, H.A., A. Al-Othman, K. Taylor, A. Al-Ghamdi, 2004. "Surface Tension of Acid Stimulation Fluids at High Temperature", *J. SPE* 43: 53-73.
- Nasr-El-Din, H.A., SPE, SPE. Al-Otaibi, A.M. Al-Aamri, A. Aramco, N.SPE. Ginest, 2005. "Surface Tension of Completion Brines", Paper SPE 93421, Presented at the SPE International Symposium on Oilfield Chemistry Held in Houston, Texas, U.S.A, February 2-4.
- Ramsay, W. and J.Z. Shields, 1893. "Physical Chemistry", 12: 433.
- Schoettle, V., H.Y. Jennings, 1986. "High-Pressure High Temperature Visual Cell for Interfacial Tension Measurements", *Rev. Sci. Inst.* 39: 386.
- Song, B., J. Springer, 1996. "Determination of Interfacial Tension from the Profile of a Pendant Drop Using Computer-aided Image Processing: 1, Theoretical", *J. Colloid and Interface Science*, 184: 64-76.
- Sugden, S., 1924. "A Relationship Between Surface Tension, Density, and Chemical Composition", *J. of the Chemical Soc.*, 1177: 125.
- William, D., Mc Jr. Cain, 1990. "The Properties of Petroleum Fluids" Pennwell Publishing Company Tulsa, Oklahoma.