Effect of Temperature and Impurities on Surface Tension of Crude Oil

Stephen Gekwu Udeagbara

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Dedication

This project is dedicated to my late sister, UDEAGBARA, BRIDGET UJU.

ACKNOWLEDGEMENT.

Table of Contents.

CHAPTER THREE (MATERIALS AND METHODS).

 CHAPTER FOUR (RESULTS AND DISCUSSION).

CHAPTER FIVE (CONCLUSION).

List of Tables.

List of Figures.

Abstract

Surface tension is one of the major issues encountered in oil industry and other works of life. This study, investigated the laboratory effect of temperature and impurities on surface tension of crude oil samples and water.

The afore-mentioned tests were carried out (in line with industrial standard) on the samples in order to determine the relationship between surface tension, temperature and impurities and also compare the variation in the measured property due to temperature and impurities. Prediction equations were also built.

The results show that surface tension decreases with increase in temperature in the crude oil samples, water and detergent while there was an increment in the presence of salt and bentonite as the concentrations increases. We also observed that surface tension increases with water-in-oil emulsion. Also, we see a strong relationship between temperature, impurities and the measured property (surface tension) with an r^2 value range of 0.7441 to 0.8638 in all the tests carried out.

This study utilized graphic and statistical illustrations to highlight the effect of temperature and impurities on the investigated property and the corresponding effect in oil industry. The collective and individual relationship between the independent and dependent variable was highlighted and variations were scientifically explained. The prediction equations serve as a quick guide to reservoir engineers to determine as the case may be the variation in the measured property from other samples of crude oil and water.

Chapter One

Introduction

1.0 Historical background of the study

The surface of any liquid behaves as if it is covered by a stretched membrane. This phenomenon is known as surface tension. Surface tension of liquid is associated to the energy required to increase its surface per unit area. It is measured in unit of force per unit length but the Cgs unit of dynes/cm is most commonly used. It has a symbol of σ *or* γ *or* τ. Surface tension depends on the nature of the liquid, the surrounding environment and temperature.

Surface tension is an effect within the surface layer of a liquid that result in a behaviour analogous to an elastic sheet. The effect of surface tension permits insects to work on water and for drops of water to bead up. When a liquid interfaces with a solid to produce this effect, it is referred to as surface tension. When this effect is found between two liquid phases, it is referred to as interfacial tension.

Surface tension results from an imbalance of molecular forces in a liquid, William, D and Mc Cain, Jr. (1990). At the surface of the liquid, the liquid molecules are attracted to each other and exert a net force pulling them together. The cohesive forces between molecules down into liquid are shared with all neighboring atoms. Those on the surface have no neighboring atom above and exhibit stronger attractive forces upon their nearest neighbor on the surface. The attractive forces produces curvature of liquid surfaces, and causes a pressure difference to exist at the curved boundary. High values of surface tension means the molecules tend to interact strongly. Lower values mean the

molecules do not interact as strongly. Surface tension is not a property of the liquid alone, but a property of the liquid's interface with another medium

Water has a very high value of surface tension because it has a high degree of hydrogen bonding. Organic molecules with polar groups such as Iodide and hydroxyl have a slightly lower surface energy than water. Pure hydrocarbons are even lower, while fluorinated compounds are very low because the fluorine atom won't share electrons very well so only dispersion interaction occurs. The surface tension of water is 72 dynes /cm at 25^0c meaning that it would take a force of 72 dynes to break a surface film of water 1 cm long at 25^0c. Hot water is a better cleaning agent because the lower surface tension makes it better "wetting agent" to get into pores and fissures rather than bridging them with surface tension.

In general, surface tension decreases with increase in temperature as cohesive forces decrease with an increase of molecular thermal activity. It vanishes at critical temperature. The influence of the surrounding environment is due to the adhesive action liquid molecules have on the interface.

Some solutes also have different effects on surface tension depending on their structure. Sugar has no effect on surface tension; inorganic salts increases surface tension; alcohols decreases surface tension; surfactants decreases surface tension and, once a minimum is reaches, no more effect. Impurities like camphor also reduce surface tension.

The interfacial or surface tension existing between a liquid and gas is required for estimating capillary pressure forces in reservoir engineering and is a parameter in some correlations used in well bore hydraulics calculations Clark, (1969). The surface tension

between natural gas and crude oil ranges from zero to about 35 dynes/cm. It is a function of pressure, temperature and composition of the phases.

In dealing with multiphase system, it is necessary to consider the effect of the forces at the interface when two immiscible fluids are in contact. When these two fluids are liquid and gas, the term surface tension is used to describe the forces acting on the interface.

Surfaces of liquids are usually blanketed with what acts as a thin film. Although this apparent film possesses little strength. It nevertheless acts like a thin membrane and resists being broken. This is believed to be caused by attraction between molecules within a given system. All molecules are attracted one to the other in proportion to the product of their masses and inversely as the squares of the distance between them. However, if the attractive forces occur at the interface between two liquids, it is called IFT (interfacial tension). IFT is an important factor in enhanced recovery processes and in reservoir engineering calculations.

Surface tension is measured in the laboratory by a Tensiometer, by drop method or by other methods. Description of these methods is given below and can also be found in most physical chemistry text.

The surface tension of a hydrocarbon mixture can be calculated if the composition of the mixture at the pressure and temperature of interest is known. The parachor of each component must also be known. The parachor is the molecular weight of a liquid times the 4th root of it's surface tension, divided by the difference between the density of the liquid and the density of the vapour in equilibrium with it. It is essentially constant over wide ranges of temperature. An equation for estimating surface tension is

$$\sigma^{0.25} = \sum_{i=1}^{c} P_{chi} \left(\frac{x_i e_L}{m_L} + \frac{y_i e_v}{M_v} \right) \text{----------------(1.0)}$$

Where δ = surface tension, dynes/cm.

P_{chi} = Parachor of ith component.

X_i = Mole fraction of ith component in liquid phase

Y_i = more fraction of ith component in vapour phase

e_L = density of the liquid phase, g/cm^3

e_v = density of the vapour phase g/cm^3

M_L = molecular weight of liquid phase

M_v = molecular weight of vapour phase

C= number of components

The parachor is a dimensionless constant characteristic of a pure compound and is calculated by imposing experimentally measured surface tension and density data on equation (1.0) and solving for $P_{(ch)}$. Fanchi, (1990) correlated the parachor with molecular weight with a simple linear equation. This linear is only valid for components heavier than methane. Fanchi's linear equation has the following form

$P_{(ch)i}$= 69.9+2.3m$_1$ ....(1.1)

Where m$_1$= molecular weight of component i

$P_{(ch)i}$ = parachor of component i

For complex hydrocarbon mixture, Katz et.al., (1943) employed the Sugden. S (1930) correlation for mixtures by introducing the components of the two phases into the equation shown below.

$$\delta^{1/4} = \sum_{i=1}^{n} \left[(P_{ch})_i \left(A_{xi} - B_{yi} \right) \right] \text{...} (1.2)$$

With the parameter A&B as defined by

$$A = e_o / 62.4Mo$$

$$B = e_g/62.4Mg$$

Where e_o = density of oil phase $1b/ft^3$

Mo = apparent molecular weight of oil phase

e_g = density of gas phase lb/ft^3

Mg = apparent molecular weight of gas phase

X_i = more fraction of component i in oil phase

Y_i = more fraction of component i in the gas phase

n = total number of components in the system

Empirical correlations in the form of graphs were presented by Baker and Swerdloff, (1962) where surface tension is correlated with temperature, API gravity, and pressure. The correlations are shown in fig 1.0.
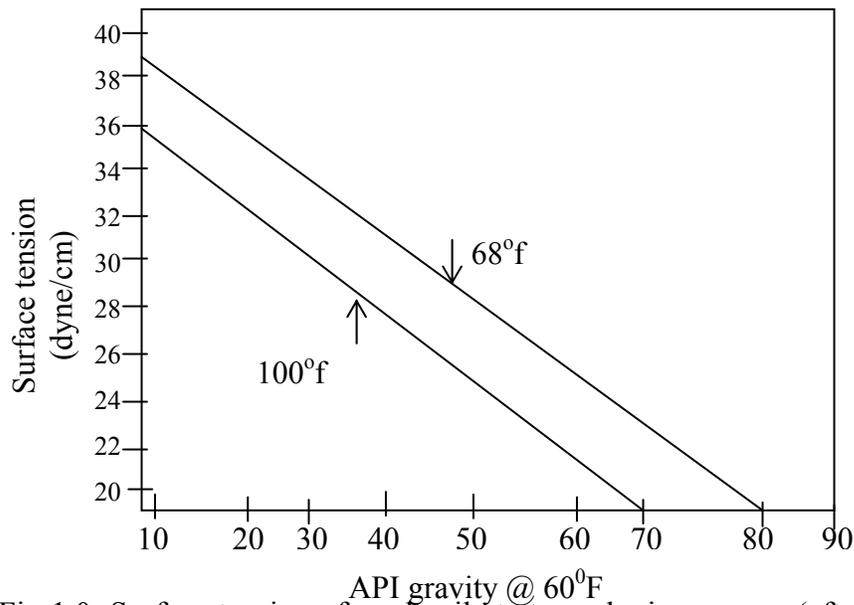
Fig 1.0: Surface tension of crude oil at atmospheric pressure (after Baker and Swerdloff ,1962).
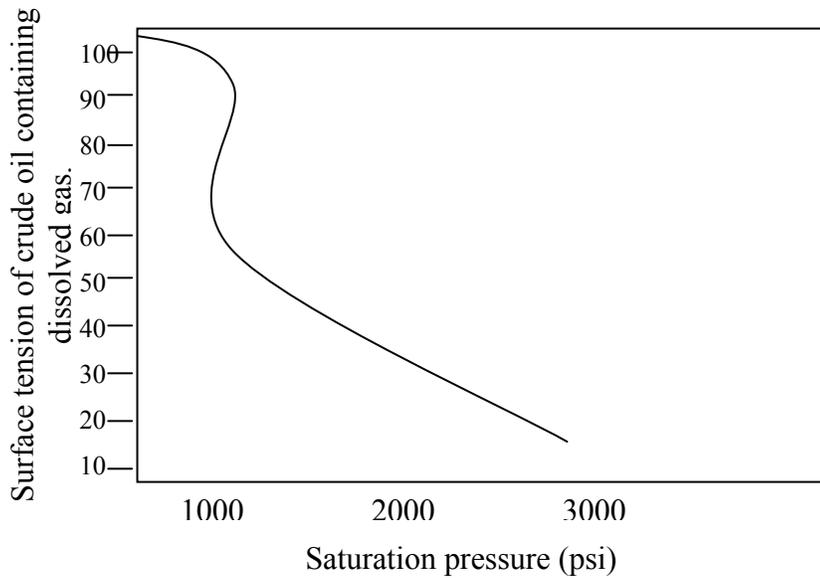
Fig 1.1: Effect of solution gas on surface tension of crude oil (after Howard, B.B and Fred, W.P, 2003).

Equations that approximate figures 1.0 and 1.1 are

$$\delta_{68} = 39 - 0.2571\gamma_{Apj} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1.3)$$

And

$$\delta_{100} = 37.5 - 0.2571\delta_{API} \quad \dots\dots\dots\dots\dots(1.4)$$

Where $\delta_{68} = IFT\ at\ 68^o\ F,\ dynes/cm$

δ_{100} = IFT at 100°F dynes/cm and

γ_{API} = gravity of stock tank oil °API'

It has been suggested that if the temperature is greater than 100°f the value of 100°F should be used. Also, if the temperature is less than 68°f, use the value calculated

6

at temperature of 68°f. For intermediate temperature, use linear interpolation between the values obtained at 68 and 100°f i.e.

$$\delta_T = \delta_{68} - \frac{(T - 68^o F)(\delta_{68} - \delta_{100})}{32} \quad ....(1.5)$$

Where $\delta_T = IFT$ at $68^o F < T < 100^o f$

The effect of gas going into solution as pressure is increased on the gas/oil mixture is to reduce the interfacial tension (IFT). The dead-end oil IFT can be corrected by multiplying it by the following correction factor.

$$F_c = 1.0 - 0.024p^{0.45} \quad ....(1.6)$$

Where P is in psia

The IFT at any pressure is then obtained from

$$\delta_0 = F_c \delta_T ....(1.7)$$

The IFT becomes zero at miscibility pressure and for most systems, this will be at any pressure greater than about 5,000 psia.

1.1 Capillary Pressure and Surface Tension

It has earlier been written that the surface or interfacial tension has the units of force per unit of length, e.g. dynes/cm, and is usually denoted by the symbol δ.

If a glass capillary tube is placed in a large open vessel containing water, the combination of surface tension and wettability of tube of water will cause water to rise in the tube above the water level in the container outside the tube as shown below (fig 1.2)
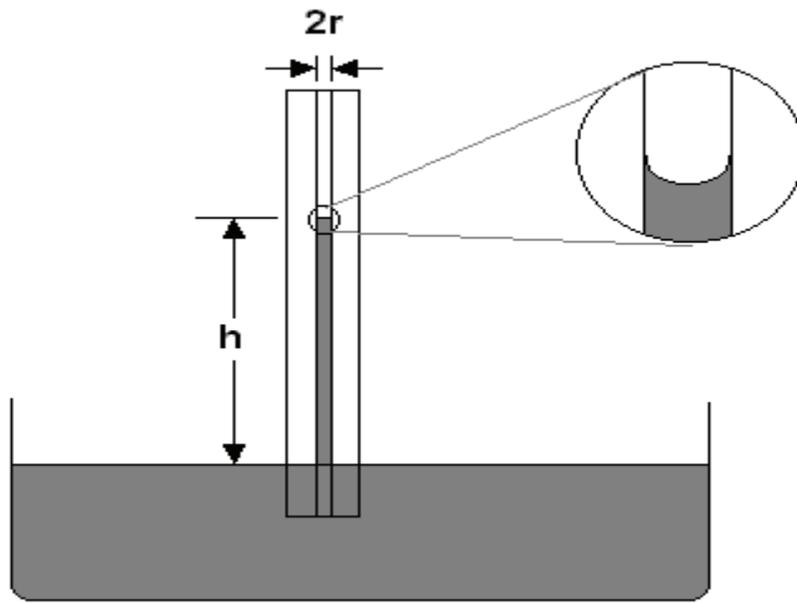
Fig: 1.2 Pressure relations in capillary tubes (after Clark, N.J, 1969)

The water will rise in the tube until the total force acting to pull the liquid upward is balanced by the weight of the column of liquid being supported in the tube. Assuming the radius of the capillary tube is r, the upward force f_{up} which holds the liquid up, is equal to the force per unit length of surface times the total length of surface or

$$f_{up} = (2\pi r)(\delta_{gw})(\cos\theta)\ldots\ldots\ldots\ldots\ldots(1.8)$$

Where δ_{sw} = surface tension between air (gas) and water (oil) dynes/cm.

θ = contact angle

r = radius, cm.

The upward force is countered by the weight of the water, which is equivalent to a downward force of mass times acceleration, or

$$F_{down} = \pi r^2 h \left(e_w - e_{air} \right) g \, \text{...................}(1.9)$$

Where h = height of which the liquid is held, cm

g = acceleration due to gravity, cm/sec^2

e_w = density of water, gm/cm^3

e_{air} = density of gas, gm/cm^3

Because the density of air is negligible in comparison with the density of water, Equation (1.9) is reduced to:

$$F_{down} = \pi r^2 \, e_w g \, \text{...................}(1.10)$$

Equation 1.8 with 1.9 and solving for the surface tension gives

$$\delta_{gw} = \frac{rhS_w g}{2 Cos\theta} \, \text{........................}(1.11)$$

The generality of equation 1.8 through 1.10 will not be lost by applying them to the behaviour of two liquids, i.e., water and oil. Because the density of oil is not negligible, equation (1.11) becomes

$$\delta_{ow} = \frac{rhg \left(e_w - e_o \right)}{2 Cos\, \theta} \, \text{.......... ....}(1.12)$$

Where e_o = density of oil gm/cm^3

e_w = density of water gm/cm^3

e_o = density of water gm/cm

δ_{ow} = Interfacial tension between the oil and the water, dynes/cm

The capillary forces in a petroleum reservoir are the result of the combined effect of the surface and interfacial tensions of rock and fluids, the pore size and geometry, and the wetting characteristics of the system. Any curved surface between two immiscible

fluids has the tendency to contract into the smallest possible area per unit volume. This is true whether the fluids are oil and water, water and gas (even air), or oil and gas. When two immiscible fluids are in contact, a discontinuity in pressure exists between the two fluids, which depend upon the curvature of the interface separating the fluids we call this pressure difference the capillary pressure and it is referred to by P_c. Collins R.E, (1990).

The displacement of one fluid by another in the pores of a porous medium is either aided or opposed by the surface forces of capillary pressure. As a consequence, in order to maintain a porous medium partially saturated with non wetting fluid and while the medium is also exposed to wetting fluid, it is necessary to maintain the pressure of the non wetting fluid at a value greater than that in the wetting fluid.

Denoting the pressure in the wetting fluid by P_w and that in the non-wetting fluid by P_{nw}, the capillary pressure can be expressed as capillary pressure = (pressure of non wetting phase) - (Pressure of wetting phase)

$$P_c = P_{nw} - P_w \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1.13)$$

That is, the pressure excess in the non wetting fluid is the capillary pressure, and this quantity is a function of saturation. This is the defining equation for capillary pressure in a porous medium.

The interfacial phenomena described above for a single capillary tube also exist when bundles of interconnected capillaries of varying sizes exist in a porous medium. The capillary pressure that exists within a porous medium between two immiscible phases is a function of the interfacial tensions and the average size of the capillaries which, in turn, controls the curvature of the interface. In addition, the curvature is also a function of the saturation distribution of the fluids involved.

1.2 Interaction of surface tension with some substances

Surface tension is a very tricky and difficult property to measure because it is influenced by so many variables and small amount of impurities have large effects. Its measurement requires rigorous experimental technique. Simple inorganic solutes at low concentration have little effect on surface tension. In fact, inorganic salts (including acids and bases) can even increase the surface tension because there tends to be lower concentration of salts at the water solution-to-air interface. Ethanol should have reduced the surface tension of the solution-to-air interface because there tends to be a large concentration of ethanol at the surface.

The mechanism for the surface tension decrease with soaps is the accumulation of an excess concentration of soap at the water-air interface, Kenneth, J.L, (1984). The soap molecules tend to align in such a way that the polar end is immersed in the water and the hydrophobic end aligns toward the air. As a result the forces holding the surface together are weakened and the surface energy decreases. Think of surface tension as the amount of energy required to stretch the surface of a liquid interface by a unit area. So in energy terms surface tension is measured in $ergs/cm^2$ (in CGS units) or numerically equivalent surface tension is the force required to increase the distance between molecules at the surface by one cm, measured in dynes/cm (in CGS units).

Air pressure does not have a major effect on surface tension; however, temperature can as earlier said.

Bile salts lower the surface tension of water because they are adsorbed at the surface. They form an adsorbed film in contrast to insoluble lipids which form spread films. When the surface is extended, the surface concentration does not change. More bile

11

salt is adsorbed from solution to cover the new surface. In contrast, in spread films the total amount stays constant and surface concentration changes. Thus, the surface tension, is the force (per centimeter) required to extend the surface (or to prevent it from shrinking), is that needed to move the required amount of bile salt out of the bulk of the solution (or to prevent it from going into the bulk of the solution). That force can be shown to vary with the logarithm of the concentration of the solution. The surface tension of bile salts is lower than that of water because the large bile salt ions adsorb at the surface. In order to adsorb, they must get there, and this involves diffusion, which is a slow process. Hence, the surface tension lowering is not instantaneous but takes some time. The more dilute the solution, the longer it takes. And since most impurities are by definition much more dilute than the bile salt of interest, they take much longer than the latter to reach the surface. Thus, it is possible to "catch" the surface tension of the bile salt by measuring surface tension after a relatively short time before some other impurities have a chance to produce much of a change.

1.3 Methods of measurement of Surface Tension

As an example, let us review, in detail, the determination of surface and interfacial tension or more properly free energy. For an interface to exist between a liquid phases, the free energy of formation of the interface must be positive. If the free energy of formation of an interface is zero or negative, the surface will tend to expand until one phase is completely dispersed in the other. In other words, the phases will be miscible. A positive free energy of formation means that a molecule at the interface is subject to a net force pulling it into its respective bulk phase.

Thus, work must be done to create each unit area of interface or

Work = ydA = ergs/cm^2

Since dA can be written as ˡdx

Work = yldx =dynes/cm

Thus, surface tension expressed as dyne/cm and surface free energy expressed as erys/cm^2 are numerically equal and dimensionally equivalent.

We will usually refer to the property as surface or interfacial tension and use the symbol γ (gamma) but when we get ready to use it in thermodynamics calculations; we will have to use it as free energy.

In determining the surface free energy, it is important to remember certain fundamental facts. Although there are several different methods for measuring the surface free energy, none of them really measure the quantity directly.

They are actually measure some other parameters, and the surface tension is calculated according to some mathematical formula. Each of these formular involves specific assumptions concerning the nature of the interface. This is not to imply that the formulas are wrong, but it does mean that the proper formular must be chosen to fit the conditions of the determination. Experimentally, methods of determining surface tension (ie vapour-liquid interfacial tension) can be classified in several ways. One consideration is whether a static or dynamic value is desired. It has been shown that in most cases attainment of surface tension equilibrium may vary from 0.6 msec for pure water to several hours or days for crude oil-brine interfaces, Blair C.M (1945).

In the case of pure liquids, equilibrium is reached quickly. Solutions, however, may take longer times. Where the value of the surface or interfacial tension equilibrates

quickly, several different experimental methods can be used; if the equilibrium is attain slowly, dynamic methods may make it possible to follow the process.

Among the static methods available are the following:

1. Capillary rise

2. Sessile drop

3. Pendant drop

4. Drop Weight (slow)

5. Maximum bubble pressure

6. Wilhelmy plate.

Examples of dynamic methods are the following:

1. Capillary waves

2. Unstable jets

3. DuNoug ring (rapid)

4. Drop weight (fast)

5. Wilhelmy plate

6. Spinning drop

For surface tension determination down to about 1 dyne/cm almost any of the methods can be used, but interfacial tension measurements can offer some experimental challenges. For the measurement of interfacial tension at values above about 1 dyne/cm the DuNouy ring, wilhelmy plate, sessile drop, or pendant drop methods can be used. For the determination of very low interfacial tensions the spinning drop method seems to be preferred.