Lecture Ten: Surface/ Interfacial Tensions & Wettability

10.1. Surface/ Interfacial Tensions

In petroleum reservoirs, up to three fluid phases, gas, oil, and water, may coexist. All these fluid phases are immiscible at the pertinent reservoir conditions. When these immiscible fluid phases in a petroleum reservoir are in contact, these fluids are separated by a well-defined interface between gas-oil, gas-water, and oil-water pairs. This particular interface is extremely small in thickness. In dealing with multiphase systems such as those encountered in petroleum reservoirs, it is necessary to consider the effect of the forces that exist at the interface when two immiscible fluids are in contact.

10.1.1. The difference between ST and IFT

The term **surface tension (ST)** is normally used when characterizing the **gas-liquid surface forces**, i.e. at the liquid surface. However, in the case of two immiscible liquids, the term **interfacial tension (IFT)** is used when describing the **liquid-liquid interfacial forces** (also between liquid and solid). Technically, in a petroleum reservoir that contains all the three phases' gas, oil, and water three different IFT or ST values are of significance: **gas-oil ST, gas-water ST, and oil-water IFT.**

10.1.2. The concept of interfacial tension or surface tension

To understand the concept of interfacial tension or surface tension, consider a system of two immiscible fluids, oil and water, as shown in Figure (10-1). An oil or water molecule, remote from the interface, is surrounded by other oil or water molecules, thus having a resulting net attractive force on the molecule of zero as it is pulled in all directions. However, a molecule at the interface has a force acting upon it from the oil lying immediately above the interface and water molecules lying below the interface. The resulting forces are not balanced because the magnitude of forces is different (i.e., forces from above



and below) and gives rise to interfacial tension and make the surface to concave to downward.

Fig. 10-1 The concept of interfacial tension (IFT) between two immiscible liquids.

Given the earlier definition of surface or interfacial tension, it has the dimensions of force per unit length usually expressed as (miliN/m) or $(10^{-3}$ N/m (dyne/cm)) and commonly denoted by the Greek symbol σ .

Despite the fact that interfacial tension or surface tension is an entirely fluidor interface-related property and not a petroleum reservoir rock property, it significantly influences other important rock properties such as wettability, capillary pressure and relative permeabilities, all of which in turn affect the recovery of hydrocarbon fluids from petroleum reservoirs.

If a glass capillary tube is placed in a large open vessel containing water, the combination of surface tension and wettability of tube to water will cause

water to rise in the tube above the water level in the container outside the tube as shown in Figure (10-2).



Fig. 10-2 Pressure relations in capillary tubes.

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 (due to gravity force) of liquid being supported in the tube. Assuming the radius of the capillary tube is r, the total upward force F_{up} (adhesive force), which holds the liquid up, is equal to the force per unit length of surface times the total length of surface, or

where:

 σ_{gw} = surface tension between air (gas) and water (oil), dynes/cm.

 θ = contact angle.

r = radius, cm.

The upward force is counteracted by the weight of the water, which is equivalent to a downward force (cohesive force) of mass times acceleration, or:

where

h = height to which the liquid is held, cm.

g = acceleration due to gravity, cm/sec².

 ρ_w = density of water, gm/cm³.

 ρ_{air} = density of gas, gm/cm³.

Because the density of air is negligible in comparison with the density of water, Equation (10-2) is reduced to:

At points 1 and 2 in Fig. (10-2):

$$F_{up} = F_{Down}$$
$$2\pi r \left(\sigma_{gw}\right)(\cos\theta) = \pi r^2 h \rho_w g$$

Equating Equation (10-1) with (10-3) and solving for the surface tension between water and gas gives:

$$\sigma_{gw} = \frac{rh \,\rho_w g}{2cos\theta} \qquad \dots \dots (10-4)$$

The generality of Equations (10-1) through (10-4) will not be lost by applying them to the behavior of two liquids, i.e., water and oil. Because the density of oil is not negligible, Equation (10-4) becomes:

$$\sigma_{ow} = \frac{rh\left(\rho_w - \rho_o\right)g}{2cos\theta}$$

..... (10-5)

where:

 ρ_o = density of oil, gm/cm³.

 σ_{ow} = interfacial tension between the oil and the water, dynes/cm.

10.2. Wettability

Wettability is the tendency of one fluid to spread on a solid surface in the presence of other immiscible fluids.

The knowledge of reservoir wettability is critical because it influences various important reservoir properties such as the distribution of gas, oil, and water within a reservoir rock, capillary pressure and relative permeability characteristics, and consequently the production of hydrocarbons.

For example, in a system comprising of oil, water (brine), and rock, (sandstone or a carbonate), one of the phases (either the oil phase or the water phase) has a tendency to preferentially wet the rock. The concept of wettability, from the very basic definition, is simple to illustrate and is shown in Figure (10-3).



Fig. 10-3 Illustration of wettability.

The spreading tendency of a fluid can be expressed more conveniently as **adhesion tension, AT**, which was first introduced by (Benner et al. in 1938). For the system shown in Figure (10-4), (oil and water system), the adhesion tension is defined by:

$$A_T = \sigma_{ow} \cos\theta \qquad \dots \dots (10-6)$$

where:

 A_T = adhesion tension.

 σ_{ow} = the interfacial tension between the denser fluid phase (water in this case) and the lighter fluid phase (oil in this case).

 θ = the contact angle.



Fig. 10-4 Schematic of a system of two immiscible liquids (oil and water) in contact with a solid surface.

The angle of contact, θ (measured through the denser liquid phase, water in this case), at the liquid-solid surface is also shown in Figure (10-4). Obviously, the value of θ will range from 0° to 180°. By definition, the cosine of the contact angle θ , adhesion tension is:

According to Equation (10-6), **positive adhesion tension** indicates that the denser phase (water in this case) preferentially wets the solid surface, whereas a **negative value of adhesion tension** indicates a wetting preference by the lighter phase (oil in this case). An **adhesion tension of zero** indicates that both phases (oil and water) have equal wettability or affinity for the solid surface. The wetting preferences indicated by the adhesion tension can also be expressed in terms of the contact angle; a 0° contact angle indicates an oil-wet system. A 90° contact angle indicates a neutral-wet system, that is, both phases have equal affinity for the solid surface.

10.2.1 Classification or Types of Wettability

A variety of wettability states exist for petroleum reservoirs, primarily depending on both reservoir fluid and rock characteristics. On a pore level, wettability in porous media has been classified as either homogeneous or heterogeneous. By definition, homogeneous means the entire rock surface has uniform wetting tendencies, whereas heterogeneous indicates distinct rock surface regions that exhibit different wetting tendencies. (Radke et al., 1992) have stated that strongly water wet, strongly oil wet, and intermediate wet systems fall under the category of homogeneous, whereas fractional and mixed-wet systems fall under the category of heterogeneous.

1- Water Wet

In this wettability state, all pore surfaces of the rock have preference for the water phase rather than the hydrocarbon phase, and as a result of this condition, the gas and oil are contained in the centers of the pores.

2- Oil Wet

This wettability state is exactly the opposite of the water-wet state, that is, the relative positions of the hydrocarbons and water are reversed.



Fig. 10-5 Schematic representation of water-wet and oil-wet pore spaces.

3- Intermediate wettability

Intermediate wettability states that in the pores there is some tendency for both phases (oil and water) to have preference for the rock surface; however, if that tendency is equal, then this may be termed as neutral-wetting state or considered as a special category of intermediate wettability.

4- Fractional Wettability

Fractional wettability states that some of the pores are water wet, while others are oil wet, or, in other words, a portion of the rock is strongly water wet, while the rest is strongly oil wet.

5- Mixed Wettability

Mixed wettability refers to a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores.

10.2.2. Methods to determine wettability

Reservoir wettability can be evaluated by two different groups of methods: **qualitative** and **quantitative**. In qualitative methods, wettability is indirectly inferred from other measurements, such as relative permeability curves. Quantitative methods are direct measurement methods, where the wettability is measured on actual rock samples using reservoir fluid samples and wettability is reported in terms of a certain wettability index, signifying the degree of water, oil wetness, or intermediate wetness. These direct quantitative methods include contact angle measurement, the Amott test, and the U.S. Bureau of Mines (USBM) wettability method.

10.2.2.1. Quantitative methods

1- Contact-Angle Method

The contact angle is the best wettability measurement method when pure fluids and artificial cores are used. Many methods of contact-angle measurement have been developed, but the most common used in the petroleum industry are sessile drop method.

It uses a single flat, polished mineral crystal (Figure 10-6). A drop of water is placed on a mineral surface in the presence of reservoir oil, and the angle through the water phase is measured. A photograph of the system is subsequently taken for accurate measurement of the contact angle

If the water drop spreads over the mineral surface, the surface is water wet and the contact angle is low; if the water drops beads up, the contact angle is high and the surface is oil wet. Contact angles ranging between 0° and 60° are considered to indicate water wetness, whereas those ranging between 120 $^{\circ}$ and 180° indicate oil wetness, and a range between 60° -75° and 105° -120° demonstrates neutral wettability of the system.



Fig. 10-6 A drop of water is placed on a mineral surface in the presence of reservoir oil

2- Amott-Harvey Relative Displacement Index

Amott carried out a test to determine the average wettability of a core which involves imbibition and forced displacement volumes both of water by oil and oil by water.

Amott's test consists of two steps:





First one involved Immersion of the core sample in oil to observe the spontaneous displacement of water by oil, the displaced water volume is recorded as V_{wsp} . Forced displacement of water by oil in the same system by

applying a high displacement pressure, the total water displaced at this step V_{wt}.

Second step involved immersion of the core sample in water to observe the spontaneous displacement of oil by water, the displaced oil volume is recorded as Vosp. Forced displacement of oil by water, the total water displaced at this step V_{ot}.

The wettability of the rock according to the Amott's test is giving by 2 ratios:

1. Displacement-by-oil index, I_o, ratio between water volume displaced by spontaneous oil imbibition alone, V_{wsp} and the total displaced by oil imbibition and centrifugal (forced) displacement, V_{wt}.

$$I_o = \frac{V_{wsp}}{V_{wt}} \qquad \dots \dots (10-8)$$

2. displacement-by-water index, I_w, ratio between oil volume displaced by spontaneous water imbibition alone, V_{osp} and the total displaced by water imbibition and centrifugal (forced) displacement, Vot

$$I_w = \frac{V_{osp}}{V_{ot}} \qquad \dots \dots (10-9)$$

The wettability of a rock is given by these indexes. The Amott-Harvey index is giving by:

..... (10-10) 0

Cuiec's Wettability Classification Based on the Amott–Harvey Wettability Index, <i>I</i> _{AH}	
I _{AH} Range	Wettability
+0.3 to +1.0	Water wet
+0.1 to +0.3	Slightly water wet
-0.1 to +0.1	Neutral
-0.3 to -0.1	Slightly oil wet
-1.0 to -0.3	Oil wet

$$I = I_w - I$$

10.2.2.2. Qualitative methods

Qualitative methods determine the degree of water or oil wetness based on: a) the shape of the curves like in relative permeability, or b) behavior of particles in fluids like in flotation methods.

1-Flotation methods

These methods work for strongly wetted systems. This method consists on placing water, oil and sand in a glass bottle, and then, they are shaken. After this, the behavior of the sand grains is observed to determine the wettability of the system. For a **strongly oil-wet** system, some of the grains will keep suspended at the oil/water interface whereas in the water, the oil-wet sand grains will group and form small oil globules coated with sand. In contrast, for a **strongly water-wet** system, clean sand grains will be observed on the bottom of the bottle, whereas some grains in the oil will group forming clumps of grains coated by thin layer of water.

2-Relative Permeability

Relative permeability methods may not notice small wettability changes in cores (from strong to moderated oil-wet or water-wet). Nevertheless, they are useful when the cores are strongly water-wet or strongly oil-wet. Craig suggested the rules of thumb to differentiate between strongly oil-wet and water-wet systems as follows (Figure 10-7):

1. Connate water saturations are usually greater than 20 to 25% PV in a waterwet system, but less than 10% PV in an oil-wet system.

2. Water saturation at which water and oil relative permeabilities intersect (are equal) is generally less than 50% for oil-wet systems and greater than 50% for the water-wet systems.

3. The water relative permeability value is much larger (from 50 to 100%) in oil-wet systems, but small values (less than 30%) in water-wet systems.



Fig. 10-7 Typical water/oil relative permeability curves

10.2.3. Factors Affecting Wettability

Reservoir wettability is almost entirely dependent on the **characteristics of the fluids involved and the lithology of the rock** in question. Obviously, these factors primarily affect the reservoir wettability. Additionally, reservoir pressure and temperature, locations (with respect to depths) of fluid contacts in the reservoir, and effect of drilling-mud filtrate invasion are also some of the factors that play a role in dictating the reservoir wettability.