A rapid method for interfacial tension calculation between rock plug and crude oil based on contact angles, application for EOR

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ABSTRACT: Interfacial tension and contact angle are two specific important parameters to take decisions for enhanced oil recovery, for instance, proper chemicals to use for surface tension reduction, expected wettability of solids, interaction between crude oil and rock. For this purpose, the article presents a method for easy calculation of the solid-liquid interfacial tension based on contact angle measurements applying Neumann's correlation and Young's equation. The main idea stands on the calculation of the rock parameters, like wettability, with known substances and extend these results to crude oils. It was possible, based on the results obtained, to establish a relationship between solid-liquid interfacial tension and contact angle for the crude oil – rock system, which can definitively be used for the calculation of interfacial tension of any other fluid spread out on the same kind of rock. A linear regression was obtained with an accuracy as good as $R^2=0.9989$. Viscosity as a function of contact angle could also be obtained for the studied crude oils in the same kind of rock.

1. Introduction

Crude oils are complex mixtures of organic molecules, some of which can be adsorbed onto high-energy surfaces, altering mineral surface wettability.(Yu and Buckley 1997) Determination of reservoir wettability and its effect on oil recover are long-standing problems in reservoir engineering. Contact angle provides a basic, and relatively fast, measure of the wetting properties of reservoir fluids with respect to selected mineral surfaces.(Morrow 1975, Morrow, Lim, and Ward 1986) A high contact angle indicates that the surface has low wetting, that means the liquid droplet will not spread very much onto the surface (Figure 1a). A low contact angle (Figure 1b,c) indicates that the surface is highly wetted, meaning that the water droplet spreads out more on the surface (hydrophilic).

Contact angle analysis is used to measure the quality of a solid surface. The surface free energy (*SFE*) is the intermolecular force created at the surface of a material, and it determines the amount of attractive or repulsive force that a surface can exert on another material on its surface. The surface tension analysis is used to measure the quality of a liquid. When talking about surface tension in relation to contact angle, there are two types of surface tension at play: the surface tension of the liquid, and the interfacial tension between the liquid and the solid. Interfacial tension is the measure of adhesive force between the liquid phase of one substance and the liquid, solid, or gas state of another substance. For reservoir fluids, interfacial tensions are expected to be affected by the presence of surface-active materials in the crude oil.(Hjelmeland and Larrondo 1986) Interfacial tension and contact angle are the specific important parameters to identify the proper chemicals for oil recovery in tertiary method.(Babu et al. 2015) Thus, it is important to have a method to calculate these interfacial

tensions prior to make enhanced oil recovery experiments, in order to know the interaction between rock and oil.

In this work, a method to calculate interfacial tension between rock and crude oil was developed. Contact angles were measured with standard fluids, and rock parameters were calculated using a thermodynamic correlation by Neumann.(Neumann and Kwok 1998, Kwok et al. 1998) Then, these parameters were used to calculate interfacial tension between crude oil and rock, using the Young's equation.

1.1. Young's equation and Neumann correlation

The Young and Laplace equations, well known for two hundred years, constitute the principles of determination of surface free energy of solids. However, in the second half of the 20th century a rapid progress in the interface science and wettability processes occurred. As a result, new calculation methods for the *SFE* determination were elaborated.(Neumann and Kwok 1998, Arsalan et al. 2013, Hao et al. 2013, Żenkiewicz 2006) Most of these methods are formulated on the basis of a previously measured contact angle (θ). (Żenkiewicz 2006, Zettlemoyer 1972, Żenkiewicz 2007) The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions: solid–vapor, γ_{sv}, solid–liquid, γ_{sl}, and liquid–vapor, γ_{lv}.(Neumann and Kwok 1998, Kwok et al. 1998) Figure 2 shows the schematic diagram for the contact angle and the interfacial tensions at the three phases boundary.

This equilibrium relation is known as Young´s equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \, Cos\theta \tag{1}$$

The measurable parameter is the contact angle θ of the liquid drop corresponding to the angle between vectors γ_{sl} and γ_{lv}. Generally, contact angle θ and γ_{lv} are known, however, γ_{sl} is mostly unknown, and therefore equation (1) cannot yet be solved for the surface energy of the solid γ_{sv}. The information regarding γ_{sl} must be independently provided, for example, by a correlation between γ_{sl}, γ_{sv}, and γ_{lv}. There are several types of correlations that have been employed and discussed in the literature.(Risović et al. 2016, Arsalan et al. 2013, Hao et al. 2013, Subedi 2011) In this work we have used the correlation proposed by Neumann and co-workers(Neumann and Kwok 1998, Kwok et al. 1998)

$$Cos\theta_Y = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}}\, e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \tag{2}$$

The solid surface energy can be determined from experimental contact angles and liquid surface tension when β is known. For a given set of γ_{lv} and θ data measured on one and the same type of solid surface, the constant β and γ_{sv} values can be determined by a least-squares analysis technique. Starting out with arbitrary values for γ_{sv} and β, iterative procedures can be used to identify that pair of γ_{sv} and β values which provides the best fit of the experimental data to the set of experimental γ_{lv} and θ pairs belonging to one and the same solid surface.(Neumann and Kwok 1998)

2. Materials and apparatuses

Carbonate rock plug under investigation is originated from northeast part of Mexico, and sandstone plug is a Berea. Core-plugs with 1.5-inch diameter were polished, cleaned with toluene and dried in an oven during 24 hours at 120°C in order to have a surface free of dirt, dust, and any contaminant. Further studies must be carried out in rough surfaces. Surface rugosity confounds visualization of a simple contact angle in a pore, because the apparent

4

contact angle (based on the average plane of the surface) can differ markedly from the true contact angle.(ZIAUDDIN et al. 2007) Petrophysical analyses were carried out in a Phi 220 Helium Porosimeter from Coretest Systems to determine grain density, porosity and pore volume. The obtained petrophysical properties are shown in Table 1.

As it can be seen from Table 1, the pore volume of carbonate rock is lower in comparison with that of sandstone rock, but regarding the porosity of carbonate it is bigger, because it presents microfractures within the rock. This should not be a factor that influence in the interfacial tension because surface is polished, however, further studies on the relation between porosity, fractures and rugosity must be carried out.(Rao and Prasad 2002, Morrow 1975) This work is mostly to lay the basis of interfacial tension calculation by the developed method.

Distilled water and toluene were used to calculate the surface free energy of rocks. The surface tension of water and toluene at 20°C was 72.75 and 28.52 mN/m, respectively.(Vargaftik, Volkov, and Voljak 1983, Jasper 1972) Three different Mexican crude oils were used to measure the interfacial tension with rock samples. Oil 1 was obtained from south part of Mexico, Oil 2 from center part of Mexico and Oil 3 from northeast part of Mexico. Their viscosity was measured with a Brookfield DV2T viscometer and their API gravity with a calibrated hydrometer. Asphaltenes were precipitated with *n*-heptane and calculated as a percentage of total oil. Properties are shown in Table 2.

For calculation of solid surface energy, contact angles were measured using a Theta Lite Goniometer and OneAttension software.

3. Results and Discussion

3.1. Surface tension of liquids

5

Surface tension of crude oils was calculated by the method of capillary rise by the following equation:

$$\gamma_{lv} = \frac{rh\rho g}{2Cos\theta} \tag{3}$$

where r is the radius of the capillary, h the height the liquid rises in the capillary, ρ the density of the liquid, g the acceleration due to gravity, and θ the contact angle with the surface, which is a correction for meniscus (Figure 3).

Results for surface tension of crude oils is reported in Table 2.

As shown above, for these crude oils, surface tension does not follow a linear relation with viscosity. Then, it implies that other characteristics rather than viscosity play an important role for the surface tension, as chemical composition.

3.2. Solid surface free energy

The most widely adopted technique for measuring contact angles is the optical-based sessile drop method. A typical goniometer consists of a horizontal stage with a solid sample mount, located between a light source and a CCD camera. A motorized liquid dosing system with microsyringe dispenses a certain amount of testing liquid onto the solid surface, forming a sessile drop. A schematic of the procedure is given in Figure 4.(Law and Zhao 2015)

After the liquid droplet contacts (wets) the surface, it spreads on it. Drop should be allowed to stabilize. For common liquids, such as water, this should take less than a second. For liquid with higher viscosity, one can monitor the dynamic of the wetting process using the video system in the goniometer. When reached static state, contact angle is obtained by curve-fitting the drop profile using the software. As different factors affect the determination of the contact angles, it is recommended to make as many repetitions as possible.

The first liquids to spread on the surface of both rocks were water and toluene. After many repetitions, an average of contact angles was obtained. With this information and known values of water and toluene surface tension, then equation 2 was used to calculate γ_{sv} and β, and equation 1 was used to calculate γ_{sl}. Results are shown in Table 3.

As observed in Table 3, sandstone rock has a slight higher hydrophobic behavior than carbonate rock, thus, the oil could be transported more easily through carbonate rock, but it doesn't happen as seen later. This proves that every system is very different from another, if having same oil but different kind of rock, the interfacial tension would vary significantly. It can also be observed that β parameter is greater for sandstone rock. Regarding solid-liquid interfacial tensions, in the case of carbonate rock there is a minimum difference between water and toluene; however, for the case of sandstone rock there is a difference of almost the half value for toluene than for water. That is the importance of this work, finding a correlation of interfacial tension between liquids spread out in the same kind of rock.

3.3. Interfacial tension

When working with oils, as viscosity is higher, the time to form a sessile droplet increases. In this work, Oil 3 has the highest viscosity and was the latest to form a sessile drop (more than an hour). In Figure 5 a curve of contact angle as a function of time for the three oils in carbonate rock is shown.

Interfacial tension was calculated when the contact angle no longer changed significantly (less than 0.5 %). Figure 6 shows initial droplet of Oil 3 and final sessile droplet after 76 minutes.

Once knowing solid–vapor (Table 3) and liquid–vapor (Table 2) interfacial tensions, the solid–liquid interfacial tensions were finally calculated. Contact angle of sessile droplets and γ_{sl} are displayed in Table 4. Even though, sandstone rock showed greater hydrophobic behavior, it showed less resistance to oils than carbonate rock. This emphasizes the importance of studying interfacial tensions separately for each system. From Table 4, it is evident that solid-liquid interfacial tension increases with contact angle.

In Figure 7. Solid-Liquid interfacial tension as a function of contact angle.Figure 7 all the fluids were graphed: toluene, Oil 1, Oil 2, water and Oil 3, for both rocks: carbonate and sandstone. Solid-liquid interfacial tension is displayed for all the fluids and it can be observed that, for the same rock, they form a linear curve. Both linear fits yielded high R-squared values, which means that, with this information, it is possible to obtain the solid-liquid interfacial tension of any other fluid (polar or non-polar) just with the measurement of contact angle of a droplet over the referred rock.

Another result obtained was the tendency of solid-liquid interfacial tension as a function of viscosity for the three oils. As viscosity increases, surface tension increases, due to higher influence of heavier fractions.

In Figure 8 the relationship between viscosity and contact angle can be observed for the three oils in carbonate and sandstone rock. This relationship follows also a linear tendency: as the viscosity increases, contact angle increases as well. In this case, the relationship definitively does not apply for polar compounds like water. It works for oils, even though they are from different regions.

4. Conclusions

Based on the experimental results the following conclusions can be drawn:

1. A method for an easy calculation of solid-liquid interfacial tension was developed using Neumann's correlation and Young's equation. With this method, parameters of rock are obtained for standard fluids and used to calculate interfacial tension of other fluids with the same rock.

2. A linear regression was obtained for solid-liquid interfacial tension as a function of contact angles for the same rock, which means that having the equation, any fluid (polar or non-polar) can be used to study the interaction with the rock.

3. Time plays an important role when having viscous fluids, since due to viscosity, it will take more time to have a sessile droplet on the surface of the rock. In the case of a very viscous fluid, such as Oil 3, it took more than one hour for the droplet to not change its shape.

4. Interfacial tension increased with viscosity for the three studied oils. A linear tendency was obtained for the three studied oils; however, this trend does not apply for polar fluids.

5. Acknowledgements

6. References

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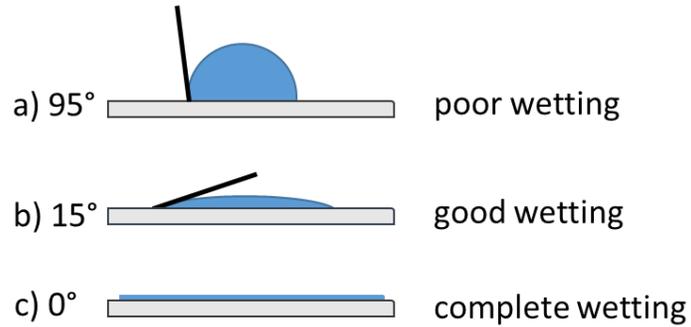*Figure 1. Contact angles for hydrophobic and hydrophilic surfaces*

Figure 2. Schematic diagram of the contact angle and interfacial tensions of the three surfaces at the three phases boundary
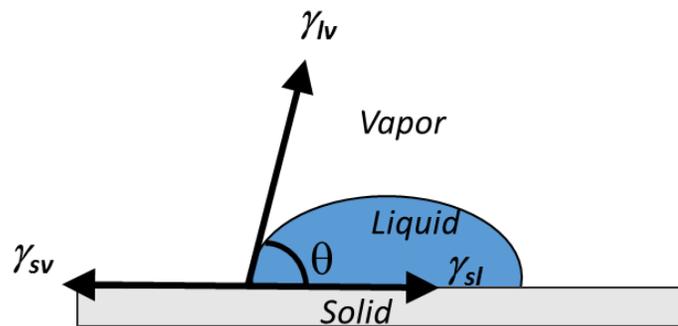

Figure 3. Measuring the surface tension of liquids with capillary rise. Toluene (left) and Oil 1 (right).
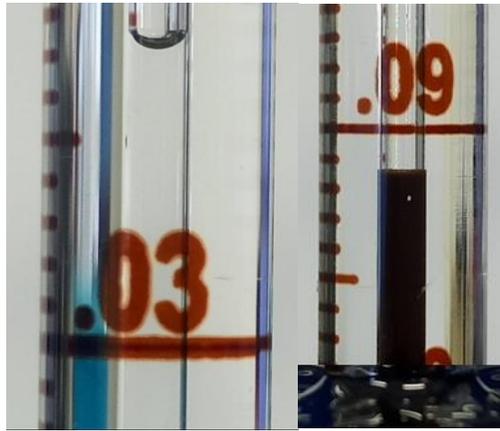
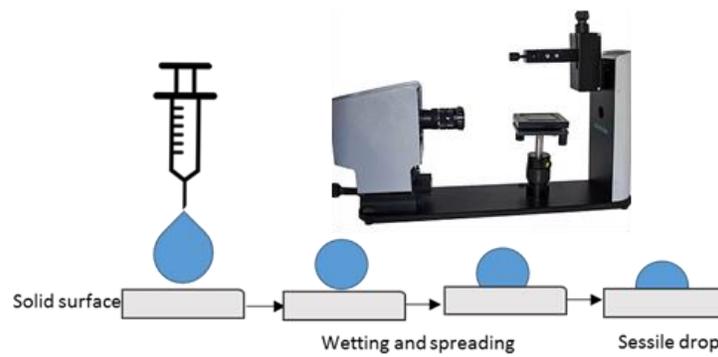*Figure 4. Formation of a sessile droplet during contact angle measurement.*

Figure 5. Time to form a sessile droplet. Oil 1(♦), Oil 2 (■) and Oil 3 (●) in carbonate rock.
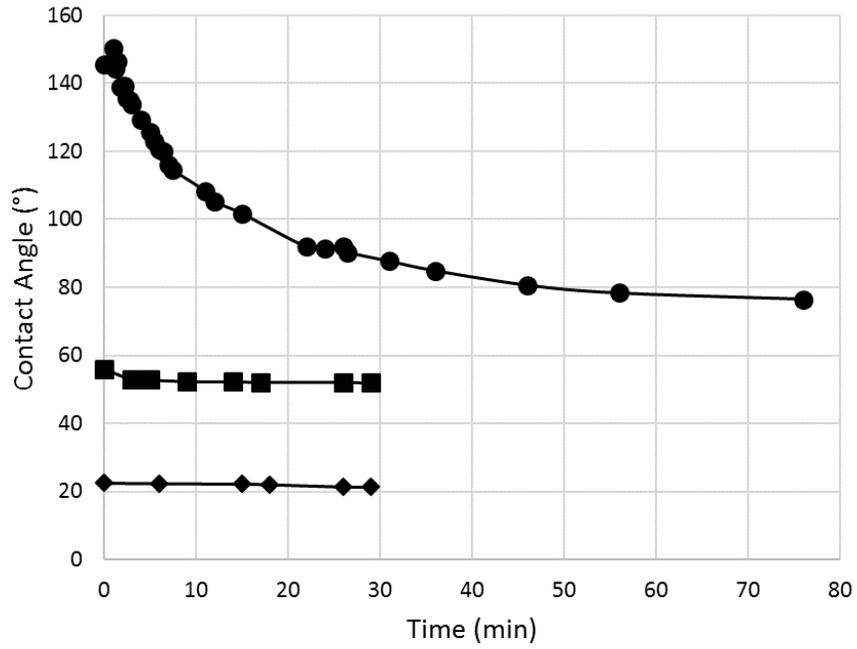
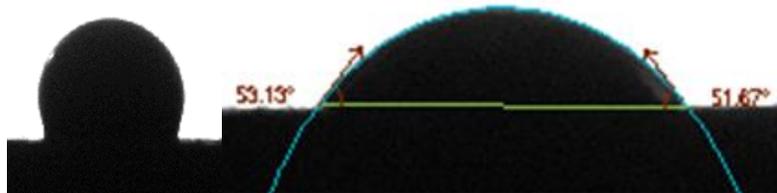*Figure 6. Initial droplet (left) and sessile droplet (right) of Oil 3.*

Figure 7. Solid-Liquid interfacial tension as a function of contact angle. Carbonate rock

sample (●), Sandstone rock sample (■), dotted lines are linear fit for each curve.
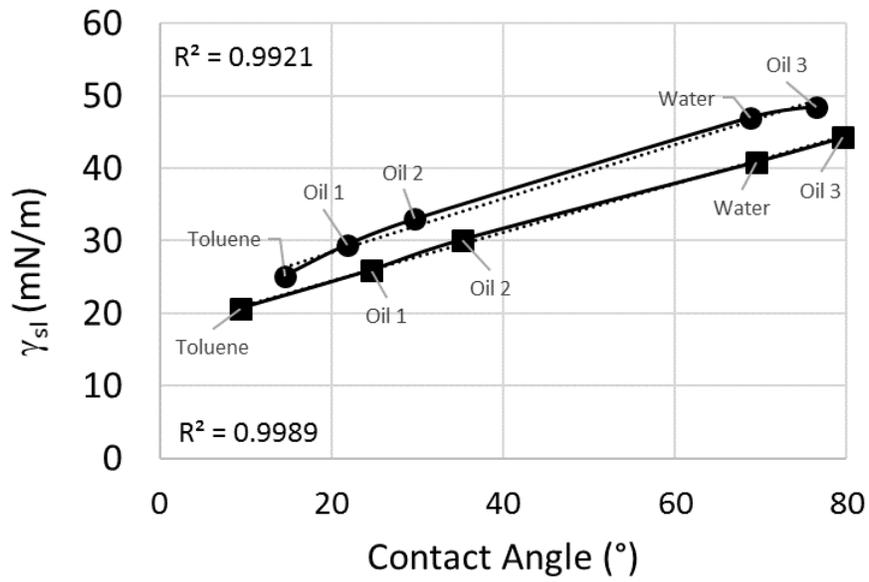
Figure 8. Viscosity of oils as a function of contact angle. Carbonate rock sample (●), Sand-

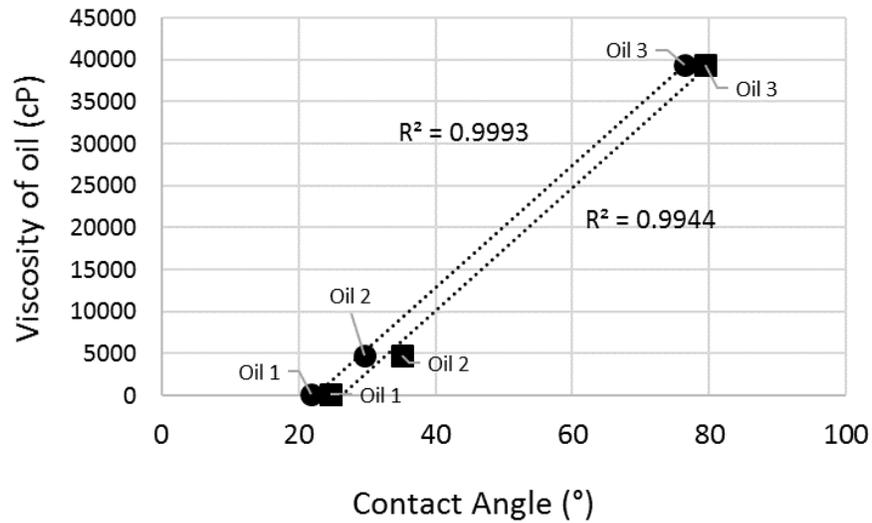stone rock sample (■), dotted lines are linear fit for each curve.

Table 1. Core properties

Properties	Carbonate	Sandstone

Pore volume (cc)	4.071	19.13
Grain density g/cc	2.677	2.58
Porosity %	16.537	5.97

Table 2.Properties of crude oils at 20°C

Crude oil	API	Viscosity (cP)	Asphaltenes %	γ_{lv} (mN/m)
1	14.1	149	10.5	25.03
2	12.3	4741	12.2	22.73
3	10.3	39,360	13.7	24.33

Table 3. Solid–vapour calculation for both rocks through water and toluene standards.

Fluid	Contact angle (°)	γ_{lv} (mN/m)	γ_{sv} (mN/m)	γ_{sl} (mN/m)
Carbonate Rock Sample				
$\beta = 0.0005529$				
Water	68.73	72.75	52.70	26.30
Toluene	14.54	28.52	52.70	25.09
Sandstone Rock Sample				
$\beta = 0.0006735$				
Water	69.4	72.75	48.70	40.81
Toluene	9.38	28.52	48.70	20.56

Table 4. Contact angles and solid-liquid interfacial tensions (γ_{sl}) for the three oils in the two rocks.

Oil	Contact Angle (°)	γ_{sl} (mN/m)
Carbonate Rock Sample		
1	21.9	29.47
2	29.71	32.96
3	76.4	46.97
Sandstone Rock Sample		
1	24.62	25.95
2	35.19	30.13
3	79.5	44.27