ABSTRACT
Surface forces between rock and fluid system play a major role in the flow characteristics of fluids in hydrocarbon reservoirs, hence, the recovery of hydrocarbons in such media. In petroleum engineering, these forces are indexed by the interfacial tension (IFT) between different phases, and the contact angle between the reservoir rock and the fluids. The evaluation and alteration of these forces are essential in planning, management and operation of reservoirs for optimum recovery.

It has been well established that the relative permeability depends on the interfacial tension at high pressure particularly at near miscibility conditions. While the interest in contact angle is its contribution to the capillary pressure as expressed by the Young-Laplace equation.

In this paper, after a brief description of the set-up used for measuring the IFT and gas-oil-solid contact angle at reservoir conditions, the variation of contact angle with pressure and IFT is discussed for four binary mixtures, namely; C1/nC4, C1/nC8, C1/nC10 and C1/nC14 and one real near critical fluid (NCF). It has been observed that the contact angle remains fairly constant for a wide range of pressure and IFT values and tend to decrease monotonically (depending on the complexity of the mixture) as the fluid approaches its critical region. This behaviour has not been reported before and could have significant implications in the management of hydrocarbon reservoirs when fluid composition is continuously changing either due to production or deliberate changes when IOR schemes are implemented.

INTRODUCTION
The capillary pressure across a curved interface is calculated by the Young-Laplace equation of the following form\(^1\):

\[
P_c = \frac{2\sigma \cos \theta}{R}
\]

The contact angle, \(\theta\), can be defined as a measure of the relative strength of adhesion of the liquid to the solid and to itself. The contact angle has a major influence on the hydrocarbon distribution.
as well as fluid in the reservoir. However there is hardly any information on the variation of gas-oil-rock contact angle with pertinent parameters in the literature.

Engineers involved in the evaluation and production of hydrocarbon reservoirs normally neglect or assume constant contact angle to calculate capillary pressure, which plays a major role in fluid flow in porous media along with viscous and gravitational forces. In many cases of improved recovery schemes, such as miscible gas injection and steam flooding, where surface forces could dominate hydrocarbon recovery, the above assumption may lead to unrealistic conclusions.

For porous media, the commonly used technique of determining the contact angles is the Washburn equation\(^3\). However, there exist other methods\(^4\) to measure the contact angle for non-porous media such as using sessil or bubble drop, whilnney plate, capillary rise, and meniscus rise. The contact angle in these methods are measured by goniometric means in equilibrium states. These methods generally cannot be applied at elevated pressure and temperature conditions which represent actual reservoir conditions.

**EXPERIMENTAL SET-UP**

Two Ruska 200cc windowed cells are mounted on a steel plate inside a temperature controlled air bath (Figure 1). The plate is connected to a mechanism, outside the air bath which allows the cells to be rocked, thereby reducing the time taken to attain phase equilibrium. The air bath controls the temperature of the cells and ancillary equipment to within ± 0.1°C of the set temperature. The pressure inside the system is maintained with two Ruska 250cc proportional mercury pumps. Equilibrium pressure is monitored by two Quartzdyne OS10K-B pressure transducers, with an accuracy of ± 1kPa each connected to one equilibrium cell.

The equilibrium cells are connected with pipework incorporating an Anton Paar 512 high pressure density cell, allowing in-situ density measurement with an accuracy of better than ± 0.001g/cc. A side tapping on each of the cells is also utilised to mount a stainless steel tube, (0.49mm outside diameter / 0.11mm internal diameter) which is used to measure interfacial tension (IFT) by the conventional pendant drop technique. Additional to the above IFT is measured by the meniscus height technique\(^7\).

Inside one of equilibrium cell a glass capillary (Figure 2) is fitted. The capillary is approximately 50mm in length and has a square internal cross section of 2mm. It is held rigidly inside the cell by Polytetrafluoroethylene (PTFE) ring.

The gas-liquid meniscus, both inside the glass capillary and inside the window of the equilibrium cell and the pendant dropper are viewed using a JVC TK-1085E colour video camera which is mounted on a macroscope which can be fitted with two objective lens. Magnifications of 50 times
and 125 times are obtained on a JVC medium resolution colour monitor. The signal from the camera is then fed through a Cortex IQ150 Image Quantifier which is used to dimension live images and those stored on a Panasonic NV-FS90 SVHS video recorder. Calibration of the viewing system is made by focusing on either a 1 mm or 2 mm stainless steel ball bearing which have been conveniently glued onto the outer surface of the cell windows. The tolerance of the ball bearings is ± 0.0025 mm.

**METHODOLOGY**

After loading the system with the fluid of interest an equilibrium pressure is selected and attained by shaking the cells. The meniscus in the cell without the capillary is then dimensioned for IFT measurement. The capillary meniscus and the height of the filaments are then measured next (Figure 3).

The density of both the vapour and liquid phases was then simply measured by pumping each phase, in turn, through the density cell. Finally, the IFT was measured by suspending a droplet of the liquid phase from the tip of the pendant dropper, surrounded by the equilibrium vapour phase.

Both pendant drop and meniscus height techniques were used for IFT measurements. Pendant drop was used for most of contact angle calculations. At low IFT (IFT<0.2 mN/m) where pendant drop failed, the meniscus height technique was used. Having obtained all necessary data, the contact angle was calculated from the following formulations:

\[
\tan \theta = \frac{R_c - \sqrt{2} R^2 - R_c^2}{\sqrt{2} \sqrt{R_c^2 + R_c \sqrt{2 R^2 - R_c^2}}} \\
\Delta Z = \frac{\sigma}{\Delta \rho g} \left( \frac{1}{R_c} - \frac{2}{R_h} \right)
\]

The parameters are identified in Figure 3.

**DISCUSSION OF RESULTS**

Figure 4 shows the measured interfacial tension for all mixtures studied at temperature of 37.8°C and various pressures. Figure 5 shows that contact angle remains fairly constant at high IFT values and monotonically decreases at low IFT values. These results could also tie-in to the relationship between density difference of liquid and vapour phases and IFT. Investigators observed that the universal critical exponent relating IFT to density difference was not constant and different exponents was needed to match their experimental data for low and high IFT regions. This observation reasonably agree with start of contact angle deline as in figure 5.
CONCLUSIONS
1- The experimental set-up employed is capable of measuring gas-oil-rock contact angle at reservoir conditions.
2- The contact angle is fairly constant at high IFT values and then declines at a variable rate depending on the volatility of the mixture.
3- The start of contact angle decline reasonably agrees with the deviation of IFT vs density difference from a single line fit.
4- The contact angle must be integrated when transposing laboratory capillary pressure data to reservoir conditions, especially at low IFT regions.

DEFINITION OF SYMBOLS

\( P_c \) \hspace{1cm} \text{capillary pressure across curved interface}
\( \sigma \) \hspace{1cm} \text{interfacial (surface) tension (IFT)}
\( g \) \hspace{1cm} \text{acceleration due to gravity,}
\( \theta \) \hspace{1cm} \text{the contact angle between the liquid and solid surface, phase,}
\( R \) \hspace{1cm} \text{the capillary tube radius (} R = r_s \cos \theta \text{),}
\( \rho \) \hspace{1cm} \text{fluid density}
\( R_t \) \hspace{1cm} \text{radius of curvature at the top of the liquid filament,}
\( R_c \) \hspace{1cm} \text{radius of curvature of the corner of the square capillary,}
\( R_b \) \hspace{1cm} \text{radius of curvature of the liquid meniscus,}
\( \Delta Z \) \hspace{1cm} \text{liquid filament height, measured from the top of the meniscus}

REFERENCES


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Figure 2 - Schematic Diagram of the VLE Rig.

Figure 3 - PVT Cell Hosting Pendant Dropper and Capillary Tube

Figure 3 - Geometrical Views of Liquid Meniscus, Liquid Filament and Capillary.
Figure 4 - Interfacial Tension vs. Pressure (all Mixtures)

Figure 5 - Contact Angle vs. interfacial Tension (all Mixtures)

(Note: in both figures symbols refers to; open diamonds: a near critical fluid, dark diamonds: C1/nC8, dark circles: C1/nC14, open circles: C1/nC10 and dark triangles: C1/nC4)