

## CO<sub>2</sub> in Enhanced Oil Recovery

This application note describes improved methods for studying enhanced oil recovery and related phenomena utilizing the Attension Theta Optical Tensiometer together with the Attension High Pressure Chamber.

### Introduction

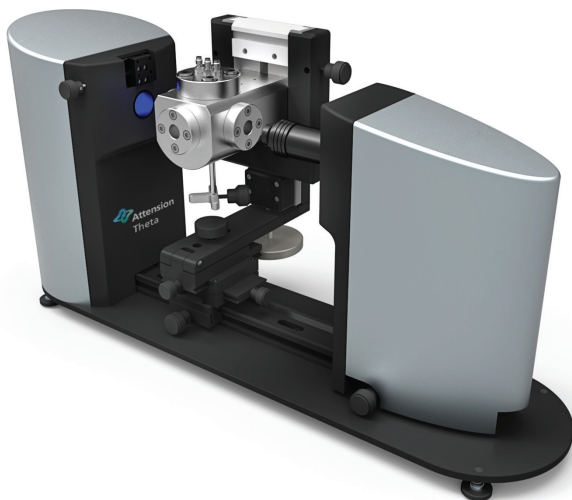
Oil reservoirs are high temperature and pressure environments that consist of porous rocks, oil, and various gases. Typically, after the primary and secondary oil recovery processes, at least 50% of the original oil still remains in the reservoir [1]. As the exploration of new oil reservoirs is decreasing because of environmental factors, there is a growing need to process the existing oil reservoirs more efficiently.

One method for recovering additional oil, termed tertiary or enhanced oil recovery, involves injecting carbon dioxide (CO<sub>2</sub>) into the reservoir, to displace and dissolve more of the remaining oil. This process can lead to an additional 8-16% recovery after the primary and secondary recovery steps [1]. The interfacial tension between hydrocarbons, water, and CO<sub>2</sub> play an important role in determining the effectiveness of the CO<sub>2</sub>-enhanced oil recovery.

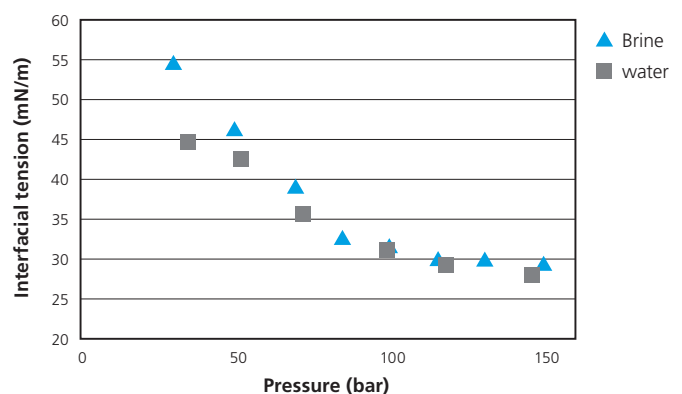
### Case study 1: Analysis of the interfacial tension between brine and CO<sub>2</sub> at elevated temperatures

Interfacial tension (IFT) between brine solutions and CO<sub>2</sub> was measured and compared to water/CO<sub>2</sub> IFT values. Measurements were performed at constant temperatures (45°C) at which CO<sub>2</sub> is in supercritical state when the pressure is increased above 74.3 bars. In this state, CO<sub>2</sub> has both gas-like and liquid-like properties and is able to dissolve hydrocarbons. Brine concentration of 35,000 ppm was selected to match the salinity of sea water.

In Fig. 2, the interfacial tension between brine/CO<sub>2</sub> and water/CO<sub>2</sub> are presented. In both cases the interfacial tension decreases as a function of pressure, plateauing at around 28 mN/m. At low pressures the interfacial tension between brine/CO<sub>2</sub> is higher than that of water/CO<sub>2</sub>. At a molecular level, this could be explained by ions that are excluded from the CO<sub>2</sub> phase that have a negative affinity towards the interface and are thus less abundant in the bulk aqueous phase. This will lead to an ionic charge gradient near the interface and enhance the attraction of water molecules towards the bulk amplifying the interfacial tension. The results are in good agreement with previously published data for these systems [2, 3].



[Figure 1] Attension Theta with High Pressure Chamber.

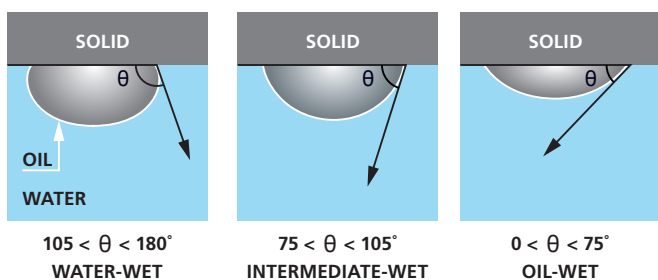


[Figure 2] Interfacial tensions between brine/CO<sub>2</sub> (triangles) and water/CO<sub>2</sub> (squares) as a function of pressure.

## Case study 2: Contact angle measurements between crude oil, brine, sandstone rock and CO<sub>2</sub>

Wettability of rock-fluid systems has been characterized by the Amott test, the U.S. Bureau of Mines tests (USBM), and through contact angle measurements. In the Amott test, an oil-saturated core sample is placed on a measuring cell filled with brine solution and the amount of oil extracted is measured. The USBM test on relies on capillary pressure curves obtained by centrifuge method. Both the Amott and the USBM methods are limited in that they provide a quantitative value of the wettability of a core *only* at atmospheric conditions. Contact angle measurements on the other hand enable the determination of the wettability of surfaces at high pressures and elevated temperatures which better mimic reservoir conditions.

Wettability has a significant effect on the efficiency of enhanced oil recovery techniques due to its effect on fluid saturation and flow behavior in porous media. There are three possible states of wettability; water-wet, intermediate-wet and oil-wet (Fig. 3). Water-wet is defined as having an oil contact angle of 105° - 180° on a rock surface surrounded by water. If the oil droplet has a contact angle of 75° - 105°, the surface is considered to be intermediate-wet. At contact angles from 0° - 75° the surface is said to be oil-wet [4].

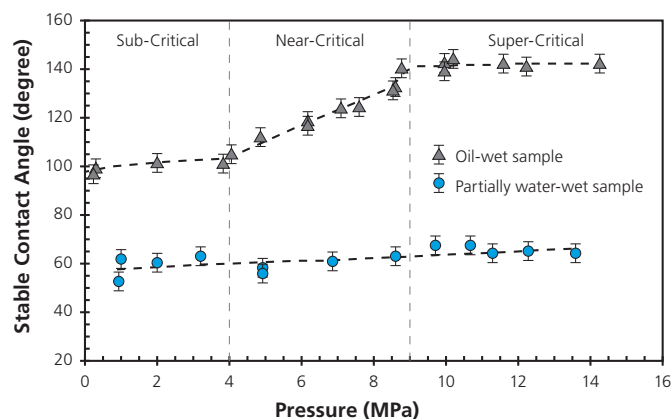


[Figure 3] Different wetting behavior of an oil droplet on a rock surface surrounded by water.

Ameri et al. studied the effect of pressure on the contact angle on oil-wet and partially water-wet rock samples [3]. The measurements were done by using the captive bubble method where a CO<sub>2</sub> bubble was placed on the sample surface in CO<sub>2</sub> saturated distilled water. The temperature was kept constant at 45°C and pressures up to 160 bars were used.

The contact angles for both samples at various pressures are presented in Fig. 4. The contact angle on the partially water-wet sample does not change significantly as a function of pressure and stays below 70°C at all pressures. On the oil-wet sample, three different regions can be identified. Below 40 bars, the CO<sub>2</sub> is in a sub-critical state and the contact angle stays fairly constant at 100° and the surface has intermediate wettability.

When the pressure increases, the CO<sub>2</sub> is near the super-critical region and the contact angle increases sharply from 100° to 140°. The substrate evolves from intermediate-wet to CO<sub>2</sub>-wet which could be due to the formation of a dense CO<sub>2</sub> layer on the solid and a large decrease in the CO<sub>2</sub> – water interfacial tension. The decrease of interfacial tension favors the contact angle to increase the area between the CO<sub>2</sub> and the water phase. At super-critical state above 90 bars, the contact angle stabilizes to 140°.



[Figure 4] Contact angles of oil-wet and partially water-wet samples as a function of pressure at a temperature of 45°C. Adapted with permission from [4]. Copyright (2013), American Chemical Society.

## Conclusions

This application note describes the two main measurement types used to study interfacial interactions and wetting behavior. Both measurements give valuable information needed in enhanced oil recovery optimization. Attension Theta together with Attension High Pressure Chamber offers a tool to study the phenomena at the pressures and temperatures equivalent to reservoir conditions.

## References

- [1] X. Li, E. Boek, G. C. Maitland, and J.P. M. Trusler, "Interfacial tension of (Brines + CO<sub>2</sub>): (0.864 NaCl + 0.136 KCl) at temperatures between (298 and 448) K, pressures between (2 and 50) MPa, and total molalities of (1 to 5) mol\*kg<sup>-1</sup>", *Journal of Chemical Engineering & Data*, 57 (2012) 1078.
- [2] B. Bharatwaj, L. Wu and S. R. P. da Rocha, "Biocompatible, lactide-based surfactants for the CO<sub>2</sub> – water interface: High-pressure contact angle goniometry, tensiometry, and emulsion formation", *Langmuir* 23 (2007) 12071.
- [3] C. Chalbaud, M. Robin, J.-M. Lombard, H. Bertin and P. Egermann, "Brine/CO<sub>2</sub> interfacial properties and effects on CO<sub>2</sub> storage in deep saline aquifers", *Oil & Gas Science and Technology – Rev. IFP*, 65 (2010) 541.
- [4] A. Ameri, N. Shojai Kaveh, E.S.J. Rudolph, K-H. Wolf, R. Farajzadeh and J. Bruining, "Investigation on interfacial interactions among crude oil – brine – sandstone rock – CO<sub>2</sub> by contact angle measurements", *Energy & Fuels* 27 (2013) 1015.