Phase boundaries under pressure

Abstract
Get up in the morning and turn the heating on, have a hot shower and put the coffee break sandwiches into a plastic bag and then off to work in the car...

Without crude oil all these pleasant things we take for granted in our daily lives would either not exist, or be much more expensive. Crude oil is one of the fossil fuels, formed several hundred million years ago. Reserves are not unlimited, and the discovery of huge new stocks of crude oil is becoming less and less frequent today, and is accompanied by ever increasing costs. This is the reason why the interest in increasing the yield of the existing crude oil reservoirs is rising. After the exploitation of crude oil deposits with primary and secondary methods, tertiary oil recovery methods are deliberately targeted at the forces that retain the crude oil in the carrier beds with the aim of increasing the mobility of the residual oil stock and achieving a total yield of considerably more than 60%. The surfactant flooding technique that is used and the optimization of this method by measuring the interfacial tension at high temperatures and pressures using a special pressure chamber developed by KRÜSS is described below.
Surfactant flooding

The processes that occur during flooding with an aqueous surfactant solution can be divided up as follows:

1. Contacts: surfactant solution – oil and surfactant solution – rock surface
2. Wetting: the contact angle between surfactant solution, oil and rock approaches 90° or more (Fig. 1)
3. Removal of the oil from the rock with distribution into small droplets
4. Formation of a stable oil-surfactant solution emulsion / microemulsion
5. Removal of the emulsion from the reservoir and transport to the surface (Fig. 2)
6. Emulsion break-down and separation of the oil from the aqueous surfactant solution

![Fig. 1 Process of dewetting](image)

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![Fig. 2: Diagram showing tertiary oil recovery](image)

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Laboratory scale measurements

By determination of the interfacial tension between the surfactant solution and oil as well as the so-called contact angle at the three-phase contact point between the rock surface, surfactant solution and oil it is possible to make quantitative statements about the capillary pressure and therefore about the possible de-oiling process. Figure 3 shows the alteration in the contact angle and the interfacial tension when acetone is added to a wash solution.

The addition of acetone to an aqueous flooding solution has the effect of lowering its interfacial tension to oil. From Young’s equation it is known that as the interfacial tension decreases the contact angle also decreases. This improves wetting by the aqueous flooding solution and therefore increases the “washing effect”.

![Fig. 3: Alteration to the interfacial tension and contact angle on a silicate base as the acetone content increases](image)

The measurements described above were made at ambient temperature and pressure and therefore do not represent the real conditions in the oil deposits. Here at times the prevailing pressures and temperatures, under which gases may also be subjected to inclusion, mean that the adhesion and wetting conditions of the oil with respect to the rock are unknown. This means that the measurement of the interfacial tension and the contact angle under the real oil deposit conditions (high pressure, high temperature) is unavoidable.

Measuring the interfacial tension under high pressures

In earlier studies the measurement of the interfacial tension under oil deposit conditions (high pressure, high temperature) was not carried out. Such a study requires the use of special measuring cells that can resist pressures of up to 700 bar at temperatures of more than 100°C. For technical reasons concerning the apparatus the measurement must be contactless. In this case the determination of the interfacial tension from the shape of a pendant or sessile drops presents itself.

A high-pressure measuring cell for pressures up to 700 bar (Figs. 4 and 5), through which the liquid-liquid system could be observed, was used for the measurements. This high-pressure measuring cell was combined with the Drop Shape Analyzer – DSA100 from KRÜSS GmbH (Fig. 4).
Figure 5 shows the measuring apparatus consisting of a high-pressure measuring cell and the Drop Shape Analyzer – DSA100 (both from KRÜSS GmbH). This arrangement can be used for measurements under pressures up to 700 bar (10 000 psi) and temperatures up to 200°C.

![Measuring apparatus](image)

The determination of the interfacial tension from the data of the digitized drop contours was carried out by adaptation of Laplace’s equation, which describes the difference in pressure over curved phase boundaries as a function of the radius of curvature and the interfacial tension. Software developed by KRÜSS and marketed under the name DSA (Drop Shape Analysis) allows the operator-friendly evaluation of the recorded drop images. Figure 6 shows values for the interfacial tension in a water – oil system as a function of the pressure. In addition, the effect the of gas inclusions often encountered in crude oil deposits on the interfacial tension is obvious (see the water – CO₂ and oil – CO₂ curves).

![Interfacial tension graph](image)

**Summary**

The measuring system offered by KRÜSS, consisting of the DSA100 and a high-pressure chamber (e.g. PA3210) provides a system with which targeted selection and systematic adjustment of surfactant solutions for use under increased pressures and temperatures is possible. In this way the use of surfactants in the chemical and, in particular, the petrochemical industry can be selectively optimized.

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