

Application Note

Evaluating the efficiency of surfactants by dynamic interfacial tension measurements of brine and crude oil

Enhanced oil recovery aims to improve the yield of hard-to-access crude oil reservoirs. In order to achieve this goal, enhanced oil recovery relies on the use of surfactant solutions to reduce the interfacial tension between crude oil and the extraction fluid, typically brine. In this application note, the SVT Spinning Drop Video Tensiometer from DataPhysics Instruments is used to demonstrate how ultra-low interfacial tension can be measured and its dynamic behaviour can be analysed. The interfacial tension of brine containing an increasing concentration of surfactant is measured. The interfacial tension could be reduced from 9.165 mN/m to 0.033 mN/m by increasing the surfactant concentration from 0% to 0.1%. Additionally the time required for the interfacial tension to reach its minimum value could be reduced significantly from 45 minutes to less than ten minutes by increasing the surfactant concentration from 0.01% to 0.1%.

Measurement deviceSpinning Drop Video Tensiometer



Measurement method
Spinning drop tensiometry

Measured quantities
Ultra-low interfacial tension
Dynamic interfacial tension

Environmental conditions Ambient temperature Samples Crude oil Brine Surfactant solution

Industries Enhanced oil recovery (EOR)



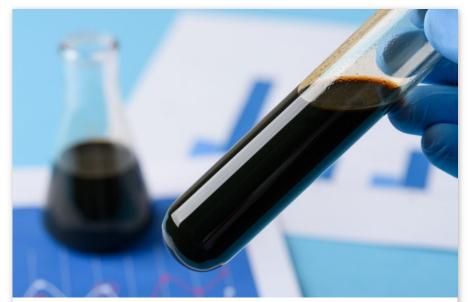


Fig. 1: Research laboratories around the globe are looking into more effective ways to recover oil from hard-to-access reservoirs for example by using surfactant solutions.

Background

Crude oil needs to be extracted from increasingly hard to access reservoirs. Typically, crude oil is bound to the rock matrix inside the reservoir. Enhanced oil recovery (EOR) uses various advanced techniques to increase the efficiency of the crude oil recovery process.

One of these techniques is the use of surfactant solutions^[1]. A mixture of brine and surfactant is pumped into the reservoir. For the crude oil to form a stable mixture with the brine, the interfacial tension between the two liquids has to be extremely low. The surfactant lowers the interfacial tension between brine and crude oil.

Additional factors, which influence the stability of the oil-brine-emulsion, are the temperature, pH-value, salinity, and pressure in the reservoir.

The interfacial tension between brine and oil does not decrease instantaneously to its minimum when the surfactant is added, since it takes time for the surfactant in the solution to migrate to the interface^[2]. A fast decrease in interfacial tension is beneficial to higher throughput rates.

In the following, the dynamic interfacial tension of crude oil and brine will be measured with different surfactant concentrations using a Spinning Drop Video Tensiometer SVT 25 from DataPhysics instruments.

Technique and Method

The Spinning Drop Video Tensiometers of the SVT series (as shown in Fig. 2) are special-purpose optical instruments for measuring extremely low interfacial tensions down to 10⁻⁶ mN/m as well as interfacial rheological properties. This technique offers unrivalled possibilities for the analysis of surfactant effectiveness in the development of emulsions and in enhanced oil recovery.

The method is based on the optical contour analysis of a drop. As shown in Fig. 3, a liquid drop is placed inside

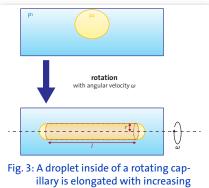


Fig. 3: A droplet inside of a rotating capillary is elongated with increasing angular velocity. Based on the elongated shape, the interfacial tension can be measured.

of a rotating capillary filled with another, denser liquid. Due to the rotation of the capillary, the centrifugal force pushes the denser liquid surrounding the drop outwards, while the less dense drop gets pushed towards the rotational axis. The drop is deformed cylindrically and its interfacial area increases. The interfacial tension counteracts this area increase and thus can be determined by analysing the equilibrium drop shape that establishes itself at a rotation with constant angular velocity.

With the SVT software the interfacial tension between the liquids can be measured automatically The system can determinate low to ultra-low interfacial tensions and can map time-and temperature- dependent changes in the interfacial tension as well as interfacial rheological properties.



Fig. 2: The Spinning Drop Video Tensiometer SVT 25 from DataPhysics Instruments is designed for the measurement of ultra-low interfacial tensions

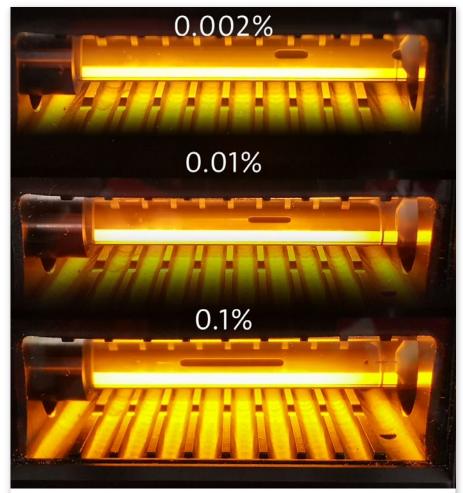


Fig. 4: The interfacial tension decreases with increasing surfactant concentration. Thus, the drop gets more elongated.

Experiment

The interfacial tension between surfactant-containing brine and crude oil was studied with an SVT 25. The brine was prepared with deionized water, NaCl at 427 mM, MgCl $_2$ at 55 mM, and Na $_2$ SO $_4$ at 27 mM. Surfactant solutions with different concentrations of the surfactant (0.1%, 0.01%, 0.002%) were prepared by adding the surfactant to the brine.

For each measurement, the surfactant solution, in this case the denser liquid, was filled in a glass capillary first. While filling the glass capillary, it is important to make sure that there are no air bubbles in the system. To facilitate the injection of the drop with lesser density (here: crude oil), DataPhysics Instruments developed a special cap for the capillary. Through a septum within the cap of the capillary, the liquid can be added using a syringe and needle. Notably, the volume of crude oil should not exceed a few µl. To ensure a high reproducibility and precision, the volume of crude oil was kept at 1 µl for each measurement in this study. After the glass capillary was prepared with the surfactant-brine-solution and crude oil, the capillary was mounted into the measurement cell using the fast-exchange capillary system of the SVT.

During the measurement, a suitable magnification was chosen to ensure

the drop was visible. With the automatic and software-controlled tilting of the measurement cell, the drop was held in a stationary position. In addition, the drop can be automatically held in the centre of the field of view, by automatic drop-shape-recognition and camera-movement to compensate for any remaining drift of the drop. Hence, long term measurements lasting several hours or even days are possible.

The rotational speed of the capillary was chosen to be so high, that the influence of the buoyant force on the shape of the drop was negligible. By knowing the rotational speed and liquid-specific data like density and refractive index, the interfacial tension can be automatically calculated by the SVT software.

Results & Discussion

Fig. 5 shows the interfacial tension as a function of surfactant concentration. Without any surfactant, the interfacial tension between brine and crude oil is 9.165 ± 0.092 mN/m. With a surfactant concentration of 0.002%, the interfacial tension decreases to 3.273 ± 0.068 mN/m. Increasing the surfactant concentration to 0.01% led to a interfacial tension of $0.044 \pm .002$ mN/m. Further increasing the surfactant concentration to 0.1% resulted in just a slightly lower interfacial tension between brine and crude oil, namely $0.033 \pm .001$ mN/m.

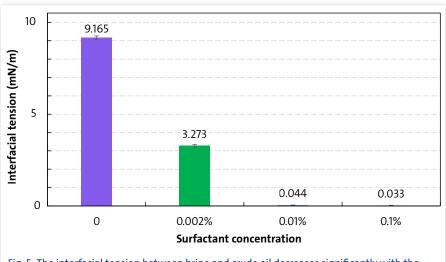


Fig. 5: The interfacial tension between brine and crude oil decreases significantly with the addition of surfactant. However, between a concentration of 0.01% and 0.1%, the interfacial tension only decreases slightly.

Looking at the dynamic behaviour of the system gives crucial additional insights. The recorded interfacial tension over time, starting with the injection of the crude oil drop, can be seen in Fig. 6. Without any surfactant, the interfacial tension stays constant at its initial value of 9.165 mN/m. With a surfactant concentration of 0.002%. the interfacial tension decreses over 1.5 hours and plateaus at 3.27 mN/m. Increasing the concentration further leads to lower interfacial tensions, which are also reached faster. By increasing the surfactant concentration from 0.01% to 0.1%, the time needed to reach the minimum interfacial tension decreases from approximately 45 minutes to less than ten minutes.

Summary

Using a SVT Spinning Drop Video Tensiometer from DataPhysics Instruments, extremely low interfacial tensions between surfactant-treated brine and crude oil could be determined easily. At a surfanctant concentration of 0.01%, the fairly low interfacial tension of 0.044 mN/m was reached. Increasing the concentration to 0.1%, the interfacial tension only changes by 0.011 mN/m to 0.033 mN/m. However, this addition of surfactant led to a quicker reduction of the interfacial tension, from taking 45 minutes at 0.01% to less than ten minutes at 0.1%.

In conclusion, measurements with an SVT can give quick, easy to achieve and helpful insights into the behaviour of the interfacial tension between brine and crude oil and hence can be used to improve formulations and procedures used in enhanced oil recovery.

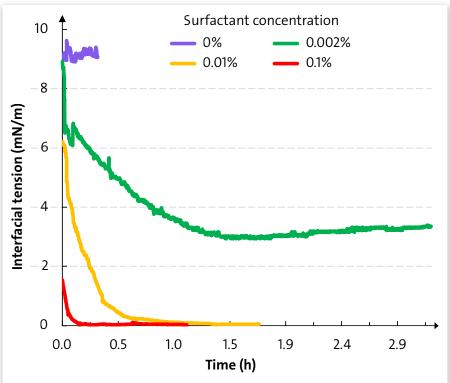


Fig. 6: Dynamic interfacial tension measurements show that the interfacial tension reaches its minimum value quicker when the surfactant concentration is increased. At a concentration of 0.1%, the minimum interfacial tension is reached within less than ten minutes.

References

- [1] Milton J. Rosen, Hongzhuang Wang, Pingping Shen, and Youyi Zhu, *Ultra-low interfacial tension for enhanced oil recovery at very low surfactant concentrations*, Langmuir **21** (2005), no. 9, 3749–3756, DOI: 10.1021/la0400959
- [2] Hooman Mohammadshahi, Hamidreza Shahverdi, and Mohsen Mohammadi, *Optimization of dynamic interfacial tension for crude oil–brine system in the presence of nonionic surfactants*, Journal of Surfactants and Detergents **23** (2020), no. 2, 445–456. DOI: 10.1002/jsde.12372

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