Developments in Green Surfactants for Enhanced Oil Recovery

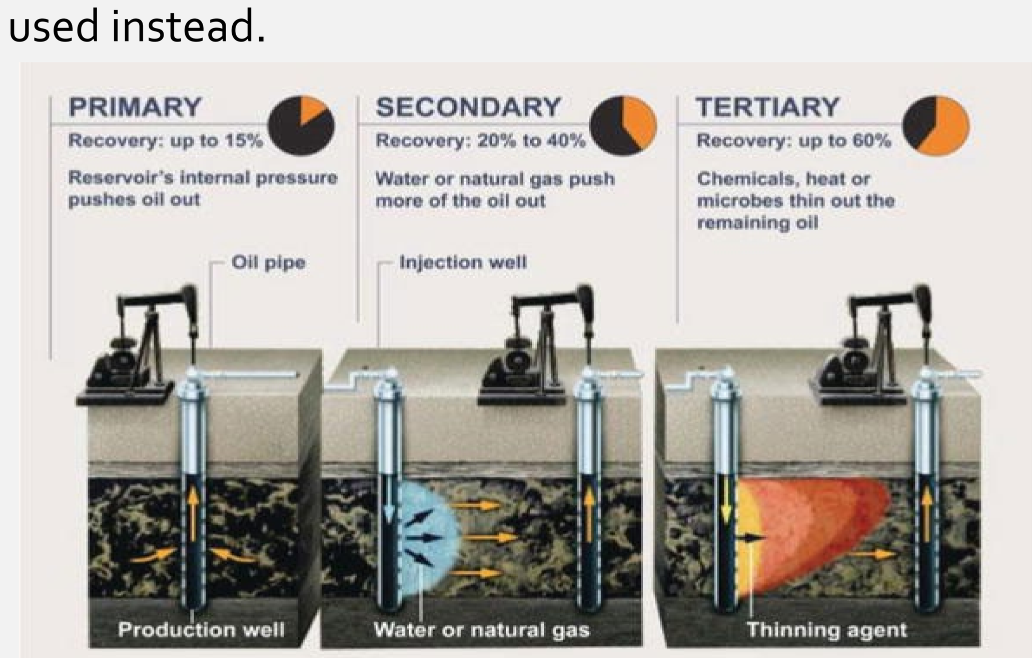
John Calderon, Raj Shah
Koehler Instrument Company, 85 Corporate Drive, Holtsville NY 11742

Overview

Despite the continuing development of sustainable sources of energy, crude oil and natural gas resources still remain crucial elements of the international economy. The oil and natural gas exploration industry alone is worth $86 trillion and represents 3.8% of the global economy. With global petroleum and liquid fuel demand continually increasing and production set to reach 99.71 million barrels per day by 2021, improving the efficiency of the extraction of what natural reserves of petroleum exist is of utmost importance as the world gradually transitions away from fossil fuels towards more sustainable sources. To that end, enhanced oil recovery (EOR) techniques have been developed and are used to maximize the amount of crude oil extracted from oil reservoirs.

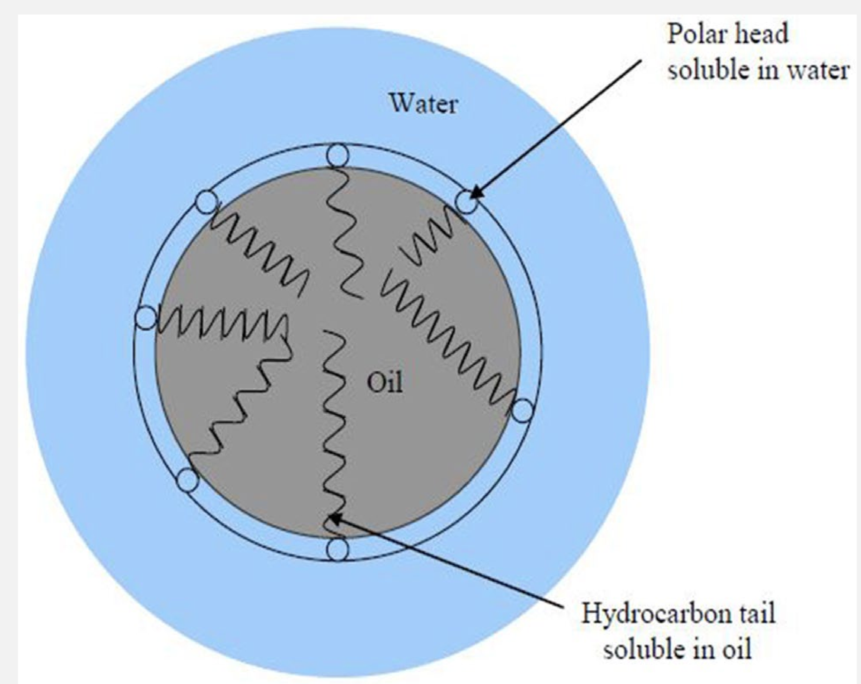
Enhanced Oil Recovery

Enhanced oil recovery (EOR) techniques contain a wide array of physical and chemical methods to maximize the extraction of crude oil from reservoirs. The most commonly applied method are the thermal enhanced oil recovery methods (TEOR) which usually involve the injection of steam or natural gas into oil wells to raise the temperature of the oil and thus lower the viscosity to allow the oil to more easily flow towards extraction sites. Such methods are known as secondary oil recovery methods and can help to improve base oil recovery from up to 15% to anywhere between 20 and 40%. TEOR techniques account for approximately 40% of EOR wells in the US and are most commonly used in the extraction of heavy oil reservoirs but are not suitable for reservoirs involving great depths and thin pay zones found in more mature reservoirs. For these situations, non-TEOR techniques such as chemical EOR are more economical and are used instead.



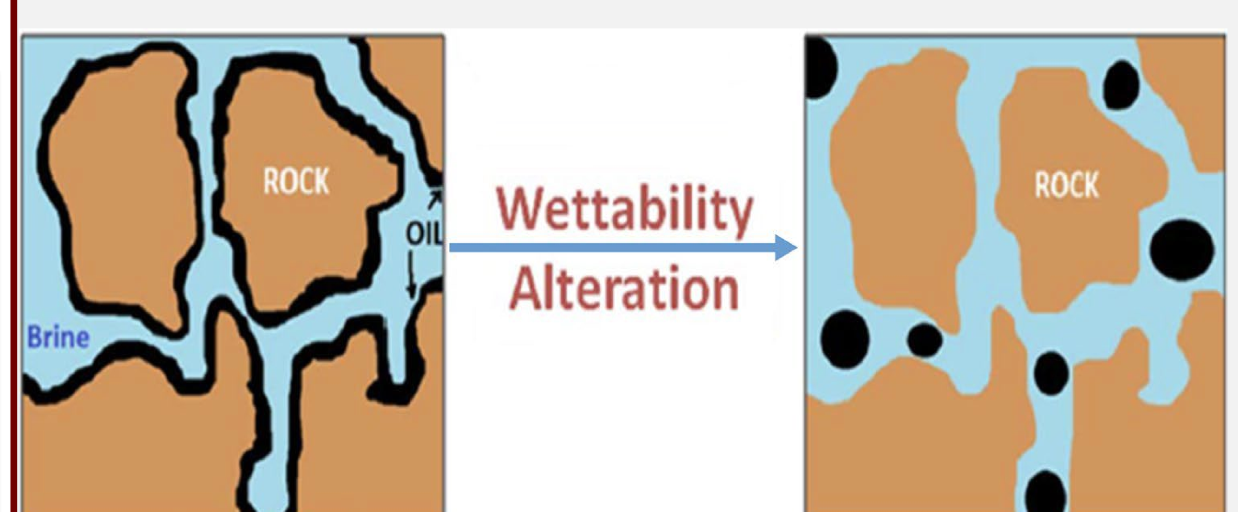
Chemical Enhanced Oil Recovery : Surfactants

IFT Mechanism on Crude Oil



Chemical EOR (CEOR) techniques are a type of non-thermal EOR technique that utilizes the injection of water-soluble chemical agents such as polymers, surfactants, alkalis, or a mixture of all of the above and have been used by EOR wells since the 1980s. In the case of surfactants, they reduce the interfacial tension (IFT) between the oil and water solution allowing greater microscopic displacement of oil through the formation of oil-water emulsions and can be used individually or in combination with other chemicals depending on the geological and economic factors of the oil well. However, the use of CEOR today is limited by high upfront capital and material costs, loss of surfactant/polymer due to adhesion to reservoir rock beds, and significant concern over the environmental impact regarding the use of polymers, surfactants, and alkalis used in CEOR techniques.

Surfactant Oil Recovery Mechanisms



The mechanisms by which surfactants improve oil recovery are known as IFT reduction and wettability alteration. The hydrophilic head and hydrophobic tail structure of surfactants work together to adsorb onto the oil/water interface thereby reducing IFT and weakening capillary forces trapping the oil within the rock pores. A separate interaction known as wettability alteration can occur simultaneously that also further improves oil recovery.

Wettability alteration alters the contact angle of oil on the rocks surface from an "oil-wet" state where the contact angle $\theta > 90°$ to a "water-wet" state where $\theta < 90°$ through desorption caused by the surfactant. The end result is a similar weakening of the capillary forces holding the oil in place and a corresponding increase in oil recovery.

Types of Surfactants for Oil Recovery

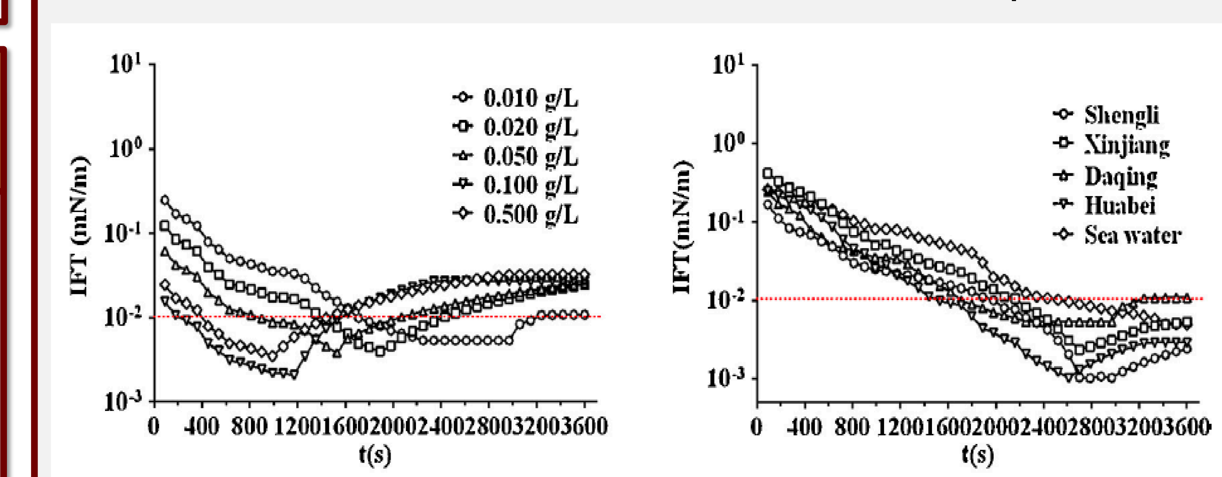
The surfactants used to activate these mechanisms can be classified into four major classes: Anionic, Cationic, Non-Ionic, and Zwitterionic. Each class represents the head structure of the surfactant referring to the charge on the hydrophilic head with anionic surfactants having a negative charge, cationic having a positive charge, non-ionic having no charge, and Zwitterionic having both a negative and positive charge. Each type of surfactant has its own particular advantages and disadvantages, but in general, anionic surfactants are the most commonly used surfactant with effective wettability alteration and IFT reduction. The choice of surfactant is dependent on the type of oil reservoir and the charge of the surrounding rocks, which is of particular importance to anionic and cationic surfactants.

Type of surfactant	Cationic	Anionic	Nonionic	Zeitterionic
Advantages	- Form stable solutions in brine - Cationic surfactants or mixtures of them with nonionic surfactants are the most effective EOR agent for carbonate reservoirs	- Effective candidate for sandstone reservoir	- Effective for surfactant flooding in formations containing high salinity water or hard water.	New generation of surfactants, has strong electrolyte tolerance, temperature resistance and thermo stability, better wetting and foaming performance
Dominant Mechanism	Reducing IFT and Wettability Alteration	Reducing IFT	Reducing IFT	Reducing IFT and Wettability Alteration

Potential of Green Surfactants

While current synthetic surfactants can be effective in their application, concern over the large scale injection of synthetic chemicals into the ground has led to research into biodegradeable "green" surfactants derived from plant oils. Current investigations take advantage of the unsaturated fatty acids or lignin in these oils to synthesize a surfactant that can surpass conventional synthetics. Of particular interest are green "zwitterionic" surfactants such as those produced by Zhang et al that have shown to achieve extremely low IFT (5.3×10^{-3} mN/m) without any extra alkali additives while maintaining strong thermal and salinity/pH resistance.

IFT vs time for Green Zwitterionic Surfactant of Oils from Multiple Reservoirs



Conclusion

While synthetic surfactants for oil recovery have long been used to assist in the extraction of oil in thin pay zones, environmental and cost concerns have led to increased attention of surfactants derived from cheap and environmentally renewable feedstocks such as vegetable/plant oils. Such surfactants are known for strong IFT reductions but require additional modification to maintain thermal/pH stability. With continued research, advancements such as green "zwitterionic" surfactants can potentially offer a cleaner and more efficient extraction of crude oil.

References

- https://www.eia.gov/outlooks/steo/report/global_oil.php
- Bachari, Zahra, et al. "Application of Natural Surfactants for Enhanced Oil Recovery – Critical Review." *IOP Conference Series: Earth and Environmental Science*, vol. 221, 2019, p. 012039., doi:10.1088/1755-1315/221/1/012039.
- Gbadamosi, A.O., Junin, R., Manan, M.A. *et al.* An overview of chemical enhanced oil recovery: recent advances and prospects. *Int Nano Lett* **9**, 171–202 (2019). https://doi.org/10.1007/s40089-019-0272-8
- https://www.energy.gov/fe/science-innovation/oil-gas-research/enhanced-oil-recovery
- https://www.intechopen.com/books/chemical-enhanced-oil-recovery-ceor-a-practical-overview/eor-processes-opportunities-and-technological-advancements
- Qi-Qi Zhang, Bang-Xin Cai, Wen-Jie Xu, *et al.*, Novel zwitterionic surfactant derived from castor oil and its performance evaluation for oil recovery, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 483, 2015, Pages 87-95, ISSN 0927-7757, https://doi.org/10.1016/j.colsurfa.2015.05.060.