

Chemical Enhanced Oil Recovery

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Abstract

Enhanced Oil Recovery (EOR) techniques are currently one of the top priorities of technological development in the oil industry owing to the increasing demand for oil and gas, which cannot be fulfilled by primary or secondary production methods. The main function of the enhanced oil recovery process is to displace oil in the production wells by the injection of different fluids to supplement the natural energy present in the reservoir. moreover these injecting fluids can alter the reservoir's properties; for example they can lower the interfacial tension (IFT) between oil and water, alter the rocks' wettability, change the pH value, form emulsions aid in clay migration and reduce the oil viscosity. In this chapter, we will discuss the following methods of chemical enhanced oil recovery: polymer flooding, surfactant flooding, alkaline flooding and smart water flooding. In addition, we will review the merits and demerits of each method and conclude the chapter with our recommendations.

Keywords: Chemical enhanced oil recovery, Polymer Flooding, Surfactant Flooding, Alkaline Flooding, Smart Water Flooding, Wettability, Interfacial tension.

Introduction

The global oil demand is growing by 2% every year. On average, 35% of the available oil in a reservoir can be produced during the primary stage of production. The remaining oil is produced by drilling more wells or by enhanced oil recovery methods. [1]

The production of oil from reservoirs has the following three stages [1]:

1. Primary recovery: includes natural depletion and artificial lift.
2. Secondary recovery: includes water flooding and pressure maintenance.
3. Tertiary recovery: includes thermal methods, gas injection, and chemical methods.
4. Other methods (i.e., bacterial and thermal).

The oil production in the secondary and tertiary stages is called improved oil recovery (IOR).

A process wherein one or more pre-selected chemicals are mixed with water and then injected into the reservoir to increase the oil recovery factor beyond water flooding levels is called chemical enhanced oil recovery (Chemical EOR). [2] Polymers, surfactants, and alkalis are most often used in chemical EOR because they can improve water/oil and gas/oil interfacial tension (IFT), microscopic and macroscopic displacement efficiencies, and bedside viscosities of water and oil. In addition, they are capable of altering the rock wettability and reducing the water-cut and water/oil ratio. [2]

EOR changes the properties of a rock/fluid system by modifying the mobility ratio or the capillary number. For example, polymers are used to enhance the macroscopic displacement efficiency by lowering the

mobility ratio, whereas surfactants are used to enhance the macroscopic displacement efficiency by increasing the capillary number. [1, 2]

Polymer Flooding

The most widely used chemical EOR method is polymer flooding. Polymers are added to injected water to increase its viscosity and maintain the mobility ratio below one, which increases the sweep efficiency and therefore the oil recovery. [3] Their capability of increasing the water viscosity leads to reduce the mobility ratio between water and oil. [1, 3]

Mobility ratio is defined as the ratio of the mobility (λ) of the displacing fluid (water) to the mobility of the displaced fluid (oil), it is calculated as permeability (κ) divided by viscosity (μ). [4]

$$M=(\lambda \text{ (water)})/(\lambda \text{ (oil)})=(K_w/\mu_w)/(K_o/\mu_o)=(K_w*\mu_o)/(K_o*\mu_w),\dots\dots\dots(1)$$

Where K_w is the effective permeability to water (mD)

μ_w is the water viscosity (cP)

K_o is the effective permeability to oil (mD);

μ_o is the water viscosity (cP).

As we can see from (Eq. (1)), volumetric sweep efficiency and mobility ratio are inversely related. To maintain “piston-like” displacement and avoid “viscous fingering,” the value of M must be less than unity [4], which means that the water viscosity must be maintained as close as possible to oil viscosity. The viscous fingering effect is highly unfavorable, as oil production sharply reduces once the viscous finger reaches the production well. [1, 4]

By polymer flooding, 30% of remaining oil can be recovered. Owing to decreased water cut in production wells, and better sweep efficiency the total cost of polymer flooding technique is less than that of water flooding. [2] The efficiency of polymer flooding ranges from 0.7 to 1.75 lb of polymer per barrel of incremental oil production. [5]

Types of polymer used in EOR

The common polymers used in EOR are [6]

1. Synthetic PAM (Polyacrylamide)
2. Partially hydrolyzed polyacrylamide (PHPAM)
3. Xanthan gum
4. Hydroxyl ethyl cellulose (HEC)
5. Guar gum
6. Sodium Carboxymethyl cellulose
7. Carboxyethoxyhydroxyethylcellulose.

Because PAM, PHPAM, and xanthan gum are the most frequently used polymers, we will discuss them in more detail.

Polyacrylamide (Figure 1) (-CH₂CHCONH₂-)

Polyacrylamide (PAM) is formed from acrylamide subunits. It can be synthesized as a simple linear-chain structure or a cross-linked structure, typically using N,N'-methylenebisacrylamide. High-viscosity aqueous

solutions can be generated with low concentrations of PAM polymers and these can be injected to improve the results of conventional water flooding. [7]

Partially hydrolyzed polyacrylamide (Figure 2)

This polymer is widely used today in EOR, and preferred for the following reasons: [4]

1. It is tolerant to high shear stresses occur during the flooding process.
2. It is not affected by bacterial attacks.
3. It has a low cost.
4. It is stable at temperatures up to 99 °C (depending on the brine hardness).
5. Some of its modified forms, such as HPAMAMPS co-polymers and sulphonated PAM, can withstand temperatures up to 104 °C and 120 °C, respectively. [5]

HPAM has high sensitivity to Brine salinity, hardness, and presence of surfactants or other chemicals have high influence on HPAM, which lower its effect in reservoirs containing salts. [8]

Xanthan gum (Figure 3)

It is used in the oil industry in large quantities to thicken drilling mud. [9] One percent of xanthan gum can significantly increase the viscosity of a liquid [10]; thus, it has excellent "low-end" rheological properties. [8] Different types of bacteria (one of which is *Xanthomonas campestris*) produce xanthan gum through fermentation of glucose or fructose. [6]

Xanthan gum Owing has a firm polymer chain and a high molecular weight; which make it is relatively insensitive to high salinity and hardness comparing with HPAM. [4] The polymer can team up with most fluid additives and surfactants used in tertiary oil recovery formulations [4], and it is stable up 90 °C; however, it is very weak against bacterial attacks when injected into reservoirs those temperature is less than 70 °C. [6]

Choosing the Best Polymer

The properties of polymers differ widely. Therefore, it is necessary to select the appropriate polymer for a particular application. It is vital to study the reservoir permeability and oil viscosity when determining the ideal molecular weight of the polymer. [5] The thermal stability of the polymer in high-salinity brine at high temperatures is also important, so the cloud point of the polymer solution must be minded. [4] Polymer retention is another essential property; it includes the possible mechanisms responsible for reducing the mean velocity of polymer molecules during their flow through porous media [4], it is endorsed to polymer adsorption. It is important to know the rock composition and polymer adsorption level to determine the best degree of hydrolysis (anionicity), because some polymers can be entrapped in a porous medium mechanically or hydrodynamically. [4, 5]

Process of polymer Flooding

The polymer flooding process includes two main stages [5], which are briefly described here.

1. Flooding of surfactants dissolved in water to reduce IFT between brine and oil and to change the rock wettability from oil wet to water wet.

2. Extended flooding of polymer dissolved in water (could extend to several years).

Polymer flooding is stopped when 30% to 50% of the reservoir rocks pore volume has been injected, and then the displacement water is pumped into the injection well to move polymer and toward the production wells. Seawater may be used as displacement water. [2]

Surfactant Flooding

Surface-active agents, usually known as surfactants [6], are chemicals those lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as cleansing agent, wetting mediators, emulsifiers, foaming agents, or dispersants. [1] Surfactants are usually organic compounds that are amphiphilic, because they contain hydrophobic groups in their tails and hydrophilic groups in their heads (Figure 4), hence, every surfactant contains an oil-soluble and a water-soluble component. When a surfactant is added to a mixture of oil and water, it diffuses in water and adsorb at boundary between air and water or at the boundary between oil and water. The oil-soluble group may extend out of the water phase into the air or into the oil phase, whereas the water-soluble head group remains in the water phase. [11]

In the bulk water phase, surfactants form combinations, such as micelles, where the hydrophobic tails form the heart of the combinations and the hydrophilic heads remain in contact with the surrounding liquid. Other types of combinations may also be shaped, such as spherical or cylindrical micelles or lipid bilayers. The shape of the combination is subjected to the chemical properties of the surfactants, such as the relative size of the hydrophilic head and hydrophobic tail, which can be determined by the hydrophilic-lipophilic balance (HLB). Surfactants decrease the surface tension of water by forming a thin film at the liquid-air boundary, and adsorbing at that interface. The mechanics of surfactant adsorption play a great role in industrial applications such as foaming, emulsifying, and coating processes, where bubbles or drops are quickly produced and must be even out and stabilized. Those mechanics are governed by the diffusion coefficient of the surfactant. After interface boundary is formed, surfactant adsorption is ruled by the distribution of the surfactant within the interface. If an energetic barrier to the adsorption or desorption of the surfactant exists, it may obstruct the adsorption rate, and the mechanics is considered “kinetically limited.” [12, 13] Energy barriers may occur because of electrostatic discharges or steric. [14] The surface rheological characteristics of the surfactant layers, including the elasticity and viscosity, has a significant impact on the stability of emulsions and foams. [15]

Classification of Surfactants

Most surfactants have same tails, they consist of a hydrocarbon chain that may be split, linear, or aromatic (Figure 5). Many surfactants include a polyether chain dismissing in a highly polarized anionic cluster. Polyether groups contain ethoxylated (polyethylene oxide-like) series inserted to increase the hydrophilic appeal of a surfactant. On the contrary, polypropylene oxides may be inserted to rise the lipophilic appeal of a surfactant. Surfactant molecules have one tail or two; those with two tails are called “double-chained surfactants”; however, in general, surfactants are categorized according to the polar head group. The non-ionic surfactants do not have any charged groups in their head, whereas the ionic surfactants carry either a positive or a negative charge on their heads. If the charge is negative, the surfactant is more specifically

called anionic; when charge is positive, then the surfactant is cationic. If a surfactant has a head with two oppositely charged groups, it is called zwitterionic.

The following are the commonly encountered types of surfactants. [16]

Anionic surfactants

Anionic surfactants are supplied with anionic effective groups at their head, just as carboxylates, sulfate, phosphate, and sulfonate.

Cationic head groups

These are pH-dependent primary, secondary, or tertiary amines; primary and secondary amines become positively charged when pH < 10. An example of a cationic surfactant is octenidine hydrochloride.

Zwitterionic surfactants

Zwitterionic surfactants possess cationic and anionic heads attached to the same molecule. The cationic head comprises primary, secondary, or tertiary amines or quaternary ammonium cations, whereas anionic head can be more flexible and may include sulfonates.

Nonionic surfactants

Nonionic surfactants possess covalently bonded oxygen-containing hydrophilic groups, which are bonded to hydrophobic parent structures. The water-solubility of the oxygen groups is the result of hydrogen bonding, which decreases with increasing temperature; consequently, the water solubility of nonionic surfactants decreases with increasing temperature. Nonionic surfactants are less sensitive to water hardness than anionic surfactants, and they foam less strongly. The differences between the individual types of nonionic surfactants are minor, and the choice is primarily governed by the costs for special properties (e.g., effectiveness and efficiency, toxicity, dermatological compatibility, biodegradability) or approval for use as a food ingredient.

The fundamental mechanism for the lowering of dynamic interfacial tension (DIT) between crude oil and water is critical to the design of a surfactant-flooding project. [3] The DIT behavior is caused by simultaneous adsorption of the auxiliary surfactant, ionized acid, and unionized acid onto the interface to form a mixed adsorption layer. [3, 17]

Surfactants form micro-emulsions when dissolved in oil or water [17], resulting in the formation of an oil bank [17]. The oil bank along with stable pressure gradient and enhanced sweep efficiency by injecting polymers will increase the oil recovery significantly. [18]

In addition to forming an oil bank, surfactants are able to change the rock wettability. [19] Wettability (Figure 6) is the tendency of one fluid to spread on or adhere to a solid surface in presence of another immiscible fluid. [20] It is given by the following equation [21]:

$$\sigma_{os} - \sigma_{ws} + \sigma_{ow} \cos \theta_c = 0, \dots \dots \dots (2)$$

- Where σ_{os} is the interfacial energy between oil and solid;
- σ_{ws} is the interfacial energy between water and solid;
- σ_{ow} is the interfacial tension between oil and water;

θ_c is the contact angle.

Wettability is determined in the following three ways [21]:

1. The contact angle measurement, or the product of the contact angle and the interfacial tension (the last term in Young's equation);
2. Measurement of the relative amounts of oil and water displaced under similar conditions;
3. Observations of displacement or surface phenomena associated with the water or oil phase.

Surfactant flooding also depends on the quality of crude oil, water salinity, and the surfactants used. Salinity plays an important role in reducing the IFT between crude oil and water. At optimal salinity (6 wt% NaCl), the IFT value for crude oil and brine system is approximately 7 mN/m, which is considerably lower than the IFT of crude oil-water system (48 mN/m). The optimal salinity also depends on the nature of the crude oil and it varies for different types of crude oils. A micro-emulsion reduces the IFT significantly up to the range of 10–3 mN/m, whereas a surfactant can reduce the IFT only up to 10–1 mN/m. [3, 20, 21]

Alkaline Flooding

To enhance oil recovery by alkaline flooding method, an alkaline chemical is injected during polymer flooding or water flooding operations. The alkaline chemicals such as sodium hydroxide, sodium orthosilicate, or sodium carbonate react with certain types of oils, and form surfactants inside the reservoir, those surfactants are able reduce the interfacial tension between oil and water and activate an increase in oil production. Alkaline flooding should not be applied in carbonate reservoirs because of the presence of calcium; hence, the mixture between the alkaline chemical and the calcium ions can produce hydroxide precipitation, and that will reduce rocks permeability and damage the formation. Some textbooks refer to alkaline flooding as caustic flooding. [9, 22, 23]

Different crude oils in different reservoir rocks can exhibit widely disparate behaviors when they come in contact with water under dissimilar environments with respect to temperature, salinity, hardness concentration, and pH. However, all researchers agree that the acidic components of crude oil are the most important factors for alkaline flooding. [3] The pH value of water for alkaline flooding should be between 10 and 12. [3, 23]

The alkali-oil reaction results in a highly oil-soluble single pseudo-acid component (HA) in oil. The alkali-oil chemistry is described by partitioning of this pseudo-acid component between the oleic and aqueous phases and subsequent hydrolysis in the presence of alkali to produce a soluble anionic surfactant A^- (its component is conventionally denoted by $RCOO^-$), as shown in (Figure 7). [24] Thus, the capillary pressures between the aqueous and oleic phases are the reduced oil-water IFT. [23] The extent of this reaction depends strongly on the pH of the aqueous solution. This reaction occurs at the water/oil interface. A fraction of the organic acids in oil becomes ionized with the addition of an alkali, whereas the rest remain electronically neutral. The hydrogen-bonding interaction between the ionized and neutral acids can lead to the formation of a complex called acid soap. [24]

Clays play a main role in the alkaline solution displacement process owing to their large surface areas. The equilibrium of ions is collapsed during alkaline flooding. Therefore, ion exchange occurs between the solid surfaces of the rocks and the alkaline solution. As the pH of the solution is getting higher, hydrogen ions on the surface react with hydroxide ions in the flooded alkali solution, thus lowering the pH of the alkaline

solution, and the base present in the alkaline solution is consumed as the alkaline solution moves in the reservoir. [24]

Mechanisms of alkaline flooding

Emulsification is an important mechanism in alkaline flooding. It is related to most other mechanisms observed in this process. The following are the key mechanisms in alkaline flooding. [24, 25]

Emulsification and Entrainment

The crude oil is emulsified in situ owing to IFT reduction, and it is entrained by the flowing aqueous alkaline solution. This mechanism requires high pH, low acid number, low salinity, and oil/water emulsion size less than the pore throat diameter.

Emulsification and Entrapment

The sweep efficiency is imposed by the action of emulsified oil droplets blocking the smaller pore throats. This mechanism requires high pH, moderate acid number, low salinity, and oil/ water emulsion size larger than the pore throat diameter. This mechanism is very important in water flooding of viscous oils, where the waterflood sweep efficiency is notoriously poor; however, no significant reduction in residual oil is expected with this mechanism.

Wettability Reversal (Oil-Wet to Water-Wet)

The oil production increases when the rock wettability is altered from oil-wet to water-wet leading to the increase in the effective permeability to oil. This mechanism is limited to oil-wet reservoirs, where wettability could be reversed from oil-wet to water-wet.

Wettability Reversal (Water-Wet to Oil-Wet)

In the reversal of wettability from water-wet to oil-wet, low residual oil saturation is attained through low IFT and the combined effects of viscous water-in-oil emulsions, which result in high capillary number. This mechanism requires high water salinity.

Preconditions for Alkaline Flooding [24]

1. Injection wells should be located within the oil zones and not in the peripheral aquifer to avoid alkali consumption caused by reaction with divalent.
2. Alkaline flooding can be executed at any development stage in reservoirs with oils having high acid numbers.
3. In reservoirs with oils having low acid numbers, alkaline flooding at an early stage yields better results. In this case, remaining oil saturation should be higher than 0.4.
4. There is no temperature limitation for alkaline flooding.
5. Alkaline consumption by chemical reaction and ion exchange is mainly due to the presence of clays. Therefore, the clay content should not exceed 15 to 25%. Formation permeability should be greater than 100 mD.
6. Oil viscosity should be less than 100 cP.

7. Formation water salinity should be less than 20%, and the divalents in the injection water should be less than 0.4%.

The following facts may be considered while designing an alkaline flooding project [1, 2, 23, 24]:

1. Alkaline consumption in the field is higher than that in the laboratory because the contact time of alkalis with rocks in the former is much longer than that in the latter.
2. Oil recovery factor in the field is generally lower than that in the laboratory.
3. Alkaline flooding is more effective when it is combined with other methods, such as polymer flooding, surfactant flooding, hydrocarbon gas injection, or thermal recovery.

Alkaline flooding has some disadvantages; the most common of them are [25]

1. Alkaline injection could cause scale problems in the reservoir, wellbore, and surface facility and equipment.
2. Stable emulsions may be formed when an alkaline solution contacts oil. This will increase the cost to treat produced fluids on the surface.

Smart Water Flooding

Smart Water flooding is injecting a chemistry-optimized water in terms of salinity and ionic composition into the reservoir. [26]

Smart water flooding has many advantages:

1. Low cost in comparison with other EOR methods.
2. It can be applied as a green-field process during the late life cycle of the reservoir and at early stages of production.

The main goal of smart water flooding is alternation of wettability. In addition to the smart water composition, level of dilution, and the underlying mechanism, the “injection scheme” is of great importance when developing a field-scale flooding project. [27]

Smart water is capable of altering the rock wettability toward lesser degree of oil-wet, and it can interact with the rock surface in a short time. [27] During tertiary recovery, the size of the smart water slug has no effect on the oil recovery. [27]

Conclusion

Chemical enhanced oil recovery is based on two basic mechanisms—increase in macroscopic efficiency and microscopic displacement efficiency.

Macroscopic efficiency can be improved by polymer flooding. Injection of polymer solution increases the viscosity of the displacing fluid and reduces the effective permeability to water.

Microscopic displacement efficiency can be improved by injection of alkali and surfactant by several mechanisms, reduction of IFT, emulsification of oil and water, solubilization of interfacial films, wettability reversal, etc.

Recovery efficiencies of different methods vary widely as the efficiencies depend on both reservoir fluid and rock properties, including reservoir pressure and temperature. The economic performance is dominated by the oil price, cost per barrel of the injected solution, and the duration of chemical injection.

Oil recovery by chemical flooding has good prospects, as most reservoirs are maturing whereas the demand for oil is increasing steadily.

Figures

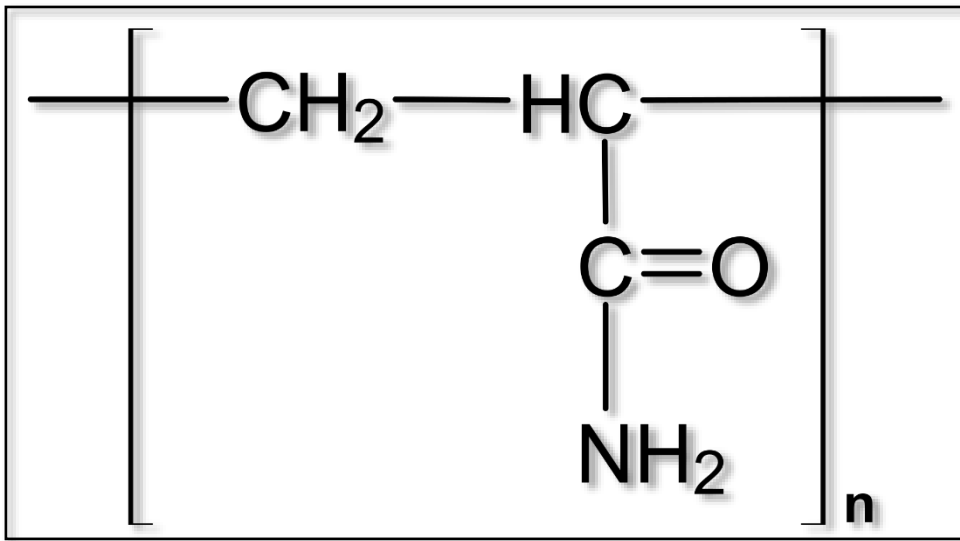


Figure 1: Polyacrylamide

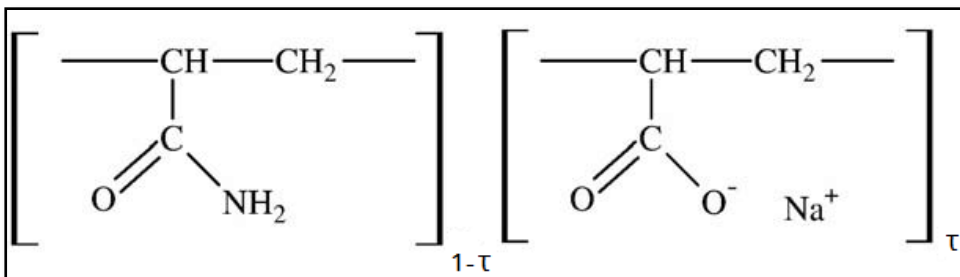


Figure 2: Partially hydrolyzed polyacrylamide (HPAM)

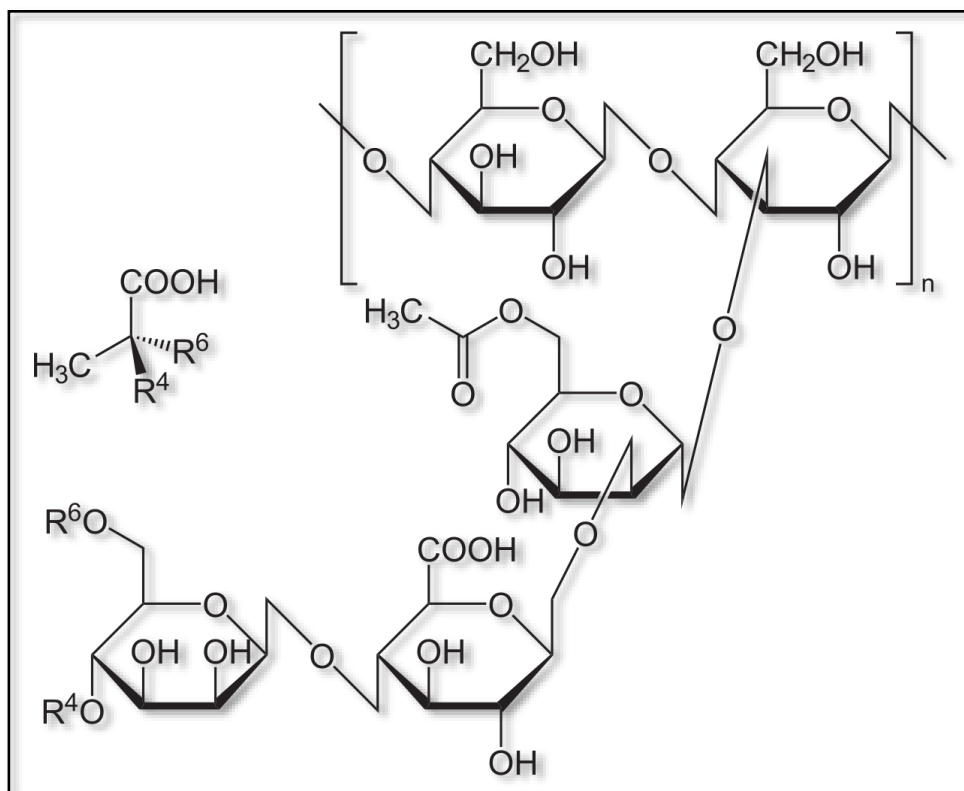


Figure 3: Xanthan gum

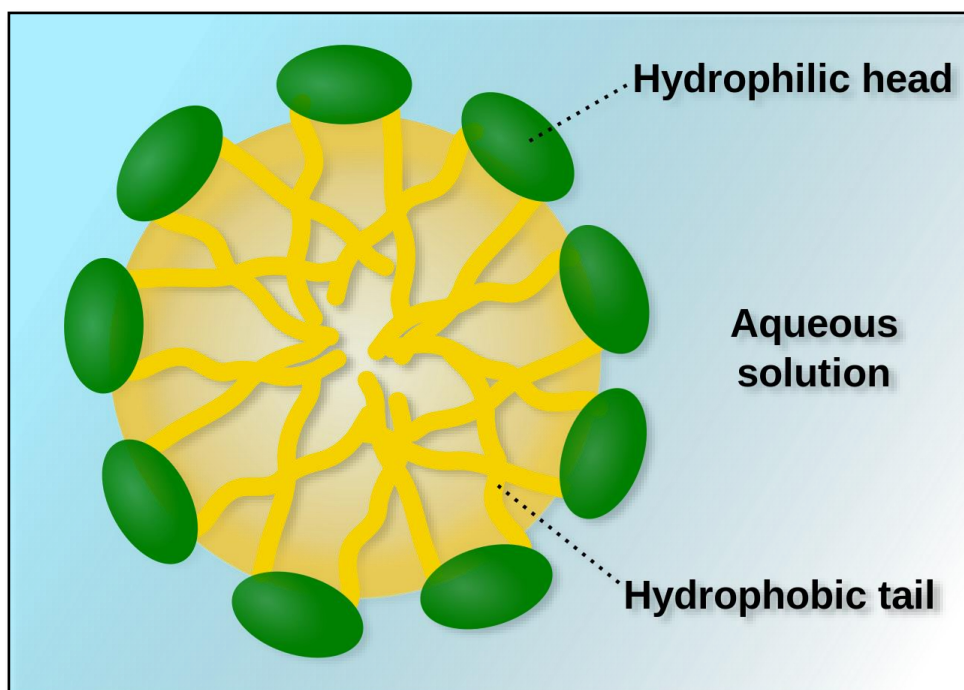


Figure 4: Schematic diagram of a micelle

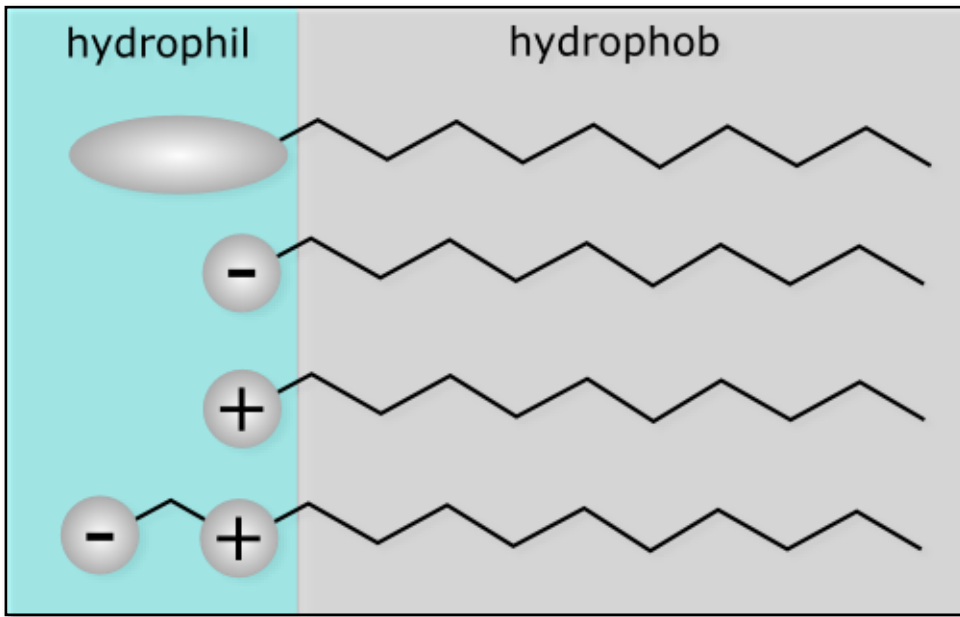


Figure 5: Surfactant classification according to the composition of the head: nonionic, anionic, cationic, and amphoteric.

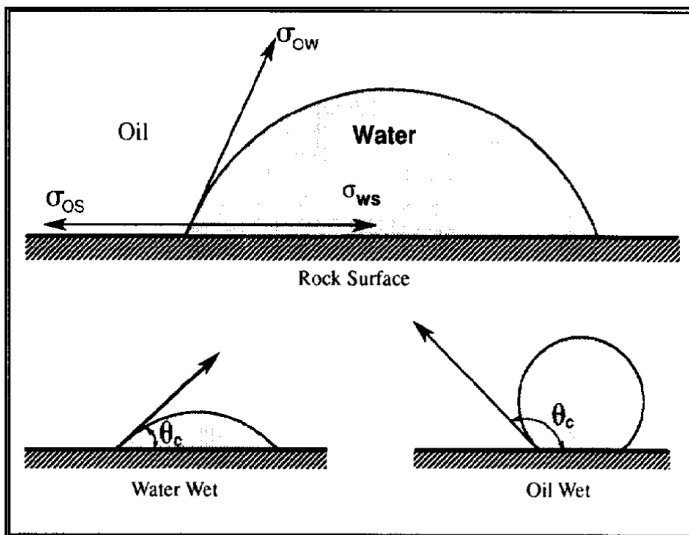


Figure 6: Wettability of oil, water, and rock system

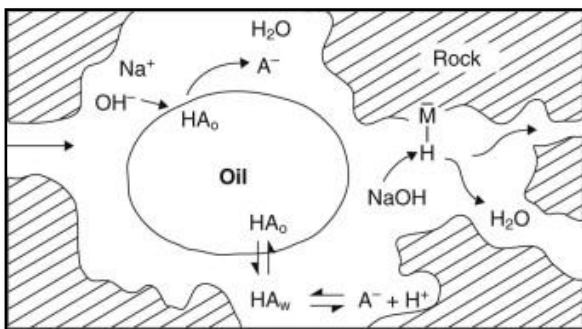


Figure 7: Schematic diagram of alkali-petroleum acid interaction

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