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Chemical EOR – High Potential beyond ASP

B. Jakobs-Sauter (Sasol Performance Chemicals), R. Rommerskirchen* (Sasol Performance Chemicals) & P. Nijssen (Sasol Performance Chemicals)

SUMMARY

Chemical enhanced oil recovery methods like alkali-surfactant-polymer (ASP) flooding can yield high additional recoveries at the right conditions. But chemical floods are often cost intensive, and are limited to certain reservoir temperatures, water salinities, and so on. These restrictions reduce the number of reservoirs where chemical floods can be applied with highest performance.

Surfactants are defined and well-known by their ability to lower the interfacial tension (IFT) between oil and water to ultra-low values and thereby mobilize the trapped oil. It is less known that due to their intrinsic properties surfactants and related chemicals can also be used to improve oil recovery via most other EOR techniques. They have the ability to decrease heavy oil viscosity, change reservoir wettability, reduce injection pressure, create stable foams, and increase miscibility. Hence, involving those materials in steam injection, gas/(sc)CO2 injection, solvent flooding, wettability alteration, or foam assisted procedures is an easy way to increase the economics of oil recovery processes even more if the injection facilities are already in place.

This paper describes the physical principles of different EOR techniques and presents examples on how to select the best surfactant for each of the above applications by considering the varying requirements and limitations.
Introduction

Chemicals like surfactants or related structures can be used in a variety of enhanced oil recovery methods. While most people – correctly – think of surfactants as substances that lower the surface or interfacial tension between two immiscible phases, some of their other physical properties are often less well known. Therefore the use of surfactants in chemical EOR is mostly associated with methods like alkali-surfactant-polymer (ASP) flooding.

This paper shows how surfactants and related chemicals can be used to improve other EOR techniques besides the typical chemical floods. While there are already some overviews on this topic [1] this paper is written from a surfactant scientist’s and manufacturer’s point of view. We will show that a deep knowledge of chemistry and physics of surfactants, their performance characteristics, and their handling properties is helpful in selecting the right “candidates” for additive testing. After a short introduction on the nature and properties of surfactants some examples of improved recovery techniques are given and the possible contribution of chemicals addition shown.

Surfactants and Related Chemicals

There is a plethora of good text books on surfactants e.g. [2, 3], and going into a detailed description here would be beyond the limits and scope of this paper. Nevertheless a short introduction might be useful to understand the basics of how to choose the right surfactant for each application.

The term “surfactant” is a contraction of “surface active agent”, describing the tendency of these chemicals to accumulate at surfaces or interfaces or self-aggregate in solution and thereby build interfaces. This behavior is driven by the amphiphilic nature of surfactants, meaning they are both water loving (hydrophilic) and oil loving (lipophilic or hydrophobic) at once. Amphiphiles have a chemical structure in which a so-called hydrophobe or tail group, usually an unpolar hydrocarbon rest, is bound to a hydrophilic head group. This head group can be nonionic or ionic in nature, but is in any case polar and water-soluble. One common classification of surfactants is in fact based on the head group, distinguishing between nonionic, anionic and cationic.

Nonionic surfactants have a head group which is polar but does not actually carry an ionic charge. Most common are so called ethoxylates, which carry multiple ethylene oxide groups in their head group. Their hydrophilicity increases with the number of EO groups, meaning that molecules with the same hydrophobe, for example a C12 carbon chain, can be oil soluble with a low degree of ethoxylation (like e.g. C12+3EO), very water soluble with a high degree of ethoxylation (like e.g. C12+9EO), and are most surface active at intermediate degrees of ethoxylation (like C12+6EO). Since the hydration of the head group decreases with increasing temperatures the water solubility of nonionic surfactants also decreases with temperature. At a certain point, the so-called cloud point temperature, phase separation between the aqueous phase and the surfactant sets in, that means the nonionic becomes water insoluble. This temperature is of course different for each surfactant structure and also depends on the salinity of the aqueous phase. Above the cloud point a nonionic surfactant does not exhibit any surface activity, on the contrary, it can e.g. act as an anti-foaming agent.

Anionic surfactants can have different head groups, such as sulfates, sulfonates or carboxylates. These differ from each other by their hydrophilicity (sulfate > sulfonate > carboxylate), by their chemical stability (sulfate < sulfonate < carboxylate), and by their tolerance against salinity (i.e. not falling out of solution in more saline brines). The latter aspect is unfortunately not very good in all three groups. This can be remedied (at least in part) by inserting ethylene oxide groups into the molecule between the carbon chain and the head group, but this also makes the molecule more hydrophilic. Alternatively (or additionally) instead of ethylene oxide one can use propylene oxide groups to increase salinity tolerance without increasing hydrophilicity. In fact the insertion of propylene oxide groups make the molecules somewhat more hydrophobic.
The hydrophobic tail group of a surfactant is usually a hydrocarbon rest, for example a linear or branched aliphatic rest (e.g. in alkyl sulfates or alcohol ethoxylates). It can also contain aromatic groups (like in alkyl benzene sulfonates or alkyl phenol ethoxylates). The influence of the tail group on the behavior of the surfactant is as important as that of the head group, in some regards even more, since the compatibility of the hydrophobe with the oil phase governs the efficiency of the surfactant. Usually, the longer the hydrocarbon chain the “stronger” the surfactant becomes, but on the other hand longer hydrophobes, especially linear ones, make the surfactant less soluble in water and tend to form mostly undesired liquid crystalline phases in solution. The addition of propylene oxide to a medium chain hydrophobe can be a way around this problem, leading to so-called extended surfactants which exhibit good interaction with oil while at the same time being more soluble and easier to handle.

The ratio of hydrophilicity and hydrophobicity of a surfactant decides if the molecule is primarily water-soluble and can therefore e.g. be used as an oil-in-water emulsifier, or primarily oil soluble, leading to water-in-oil emulsions. Surfactants with well-balanced hydrophobicity/hydrophilicity are the most surface active as they are equally well (un)-soluble in oil and in water. The overall size of a surfactant molecule on the other hand decides its main field of application: Short molecules exhibit more solvent-like traits, somewhat longer ones are usually good wetting agents, mid-chain length surfactants are most surface active and e.g. used as detergents while longer chained surfactants are used as emulsifiers or dispersants.

**Foam Flooding – Steam Foam**

In all improved or enhanced recovery methods in which the flood media used have lower densities and / or viscosities than the crude that should be mobilized problems with poor sweep efficiency due to channeling, fingering or override can be encountered. This is true in water floods but also in steam or gas flooding. Mobility control is the key to enhance the sweep efficiency, as exemplarily shown in Figure 1 for gas flooding application.

![Figure 1](image-url) *Figure 1 Enhancement of sweep efficiency in gas flood (left) by application of water-alternate-gas (WAG, middle) or foam assisted WAG (FAWAG, right) techniques.*

The leftmost picture shows problems that can arise in gas injection like viscous fingering or gravity segregation which lead to early gas breakthrough. Application of an injection pattern in which water and gas are alternated (water-alternate-gas, WAG) helps towards better sweep efficiency but is still affected by gravity segregation and reservoir heterogeneity. Addition of surfactant to the water phase (right) builds a foam which further enhances sweep efficiency by viscosity increase of the flood fluid.

As stated above foam assisted methods can also be applied in steam applications for heavy oil recovery. The challenges here are well known: Low API gravity combined with high viscosity (up to several million centiPoise) of the crude and often low permeability of rock formations make the oil essentially immobile at formation conditions. Introducing steam into heavy oil reservoirs is one of several thermal methods that try to reduce the oil viscosity and thereby mobilize it. But poor sweep efficiency is also a problem in this application and mobility control with foams could be of advantage.
The ability to build foam is of course well known for surfactants, but foaming under steam conditions poses high challenges: The surfactants have to be chemically stable to up to 300 °C or more, show foaming properties (foamability and foam stability) under these conditions, remain at the water-gas interface to ensure the mechanical stability of the foam also in contact with oil, and should have low adsorption on the rock. With these selection criteria the first candidates to look at would be anionic surfactants – known as better foamers than nonionics – but not sulfates due to their well known instability under thermal conditions. Nonionics might be suitable in terms of chemical stability, but usually form less stable foams and also are known for their upper miscibility gap, i.e. their water solubility diminishes with increasing temperature and over a certain point (the so-called cloud point) they become insoluble and effectively even act as anti-foamers.

We have tested the thermal stability for a range of theoretically suitable surfactants from the sulfonate and carboxylate type: The surfactant samples (1 wt.% in aqueous 1% NaCl solution) were incubated at 250 °C for one day or one week, respectively, in a heated pressure proof vessel and chromatographically analyzed before and after this time. Figure 2 shows HPLC chromatography traces of an alkyl benzene sulfonate (top) and an alcohol ether carboxylate. As can be seen for both surfactant types the “before” and “after” curves show virtually no difference, attesting to chemical stability under the conditions tested here.

Furthermore the foam performance of a range of surfactants was tested. The test looked at initial foam volume and foam stability in form of half life time. While we were not yet able to measure foams at 250 °C we chose at least an elevated temperature of 90 °C. 200 ml of a 0.5 wt. % surfactant solution was placed into a graduated vessel and agitated at 9500 rpm for 30 seconds. The initial foam volume generated after 30 sec. was recorded as well as the half life time, i.e. the time it took for the foam to drain to half volume.

In pure surfactant solutions (no salinity and without oil addition) the initial foam volume of typical good foaming anionic surfactants doesn’t differ much, as expected the foam volume is in most cases slightly lower at elevated temperature but not significantly so. The half life times show more differentiation, at room temperature the four carboxylates show a clear trend, but at 90 °C this ranking is partly reversed. Figure 3 shows the results of this test.

Under more realistic conditions, i.e. with different salinity brines and with an oil load on the foam system, the results now clearly differentiate. Figure 4 shows an overview: The benchmark surfactant, which was best in foam volume and half life time at room temperature and without salt and oil load, now shows a clear performance dependency on the oil carbon number in the initial foam volume, while the half life times get worse fast and go to zero at higher salinity. The alkyl benzene sulfonate clearly outperforms the benchmark and shows the overall best results under oil load at low and medium salinity, together with the carboxylate 3. At 2.5% salinity however especially the half life times show that the end of the sulfonate’s salinity tolerance is reached. Here the ether carboxylate 1 is the clear “winner” in both initial volume and half life time.
Figure 2 Chromatography traces of alkyl benzene sulfonate (top) and alcohol ether carboxylate surfactant before and after incubation at 250 °C. No degradation can be observed.

Figure 3 Initial foam volumes and foam half life times of different 0.5% surfactant solutions in demineralized water (no salinity) without oil load at 20 °C and 90°C.
Steam Assisted Gravity Drainage (SAGD)

Steam assisted gravity drainage (SAGD) is, as the name says, a specialized steam assisted recovery method. Similar to the steam injection described above also in this technique steam is injected into a heavy oil reservoir like e.g. tar sand, using the upper of two parallel horizontal wells. Contrary to what was described above the main challenge here is not the mobility control of the steam, so foaming properties is not in the list of selection criteria for a chemical additive. In this case the main purpose of the additive is to lower the interfacial tension to facilitate oil mobilization but also to further reduce the oil viscosity and if possible also keep it lower when temperatures decrease again. Similar to the case above are the challenges of thermal stability, compatibility with the formation water and the ability to vaporize under the applied conditions. Good handling properties as high flash point (which is always a concern in “traditional” solvents), low pour point (cold weather conditions) and a liquid high active supply form are a bonus in all applications.
Following from the requirements listed above the best candidates for successful additives are nonionic surfactants with short to medium chain lengths, which are known to be thermally stable and exhibit solvent like traits for viscosity reduction as well as good wetting ability to allow the water phase to wet the rock surfaces. Compared to traditional solvents short to medium chain nonionic surfactants have the additional bonus of lowering the interfacial tension between water and oil phase, making it easier overall to mobilize oil. Furthermore they have a much higher flash point than traditional solvents and are in some cases more environmentally benign.

Figure 5 Schematic overview of SAGD injection and production wells.

Several companies active in heavy oil production have already reported on the addition of surfactants or related additives in steam applications e.g. [4, 5]. Zeidani and Gupta [5] have reported lab test results showing that nonionic surfactants as described above are effective at improving oil recovery and reducing steam consumption. They exhibit suitable thermal stability at 325 °C, an incremental oil recovery factor (RF) in the range of 13% increase combined with reductions in the cumulative steam to oil ratio (SOR) in order of 11%. Figure 6 shows the results of their sand pack tests which compares steam only injection and steam with addition of 2000 ppm of different surfactants.
Wettability Alteration

Wettability alteration is the effort to turn an oil-wet reservoir into an intermediate- or even water-wet state to mobilize oil adhering to the rock. This is especially needful in carbonate reservoirs which are often strongly oil wet and also strongly fractured, making other enhanced recovery methods unsuitable. Wettability alteration can be achieved in different ways, namely thermal and chemical [6]. Chemical methods can on the one hand be anything that changes the surface charges of the formation rock, like pH alteration, low salinity, or smart water flooding. On the other hand, surfactants are well known to adsorb at and interact with surfaces; in fact, turning hydrophobic surfaces more hydrophilic is one of the base principles of hard surface cleaning.

Usually, in surfactant flooding techniques “low rock adsorption” is one of the most cited criteria; understandably since chemicals are a cost factor and loss in the reservoir should be minimized. From that standpoint one would e.g. preferably chose cationics for surfactant floods in carbonate reservoirs (which have positive surface charges) to minimize adsorption. It was found, however, that also anionic surfactants were able to deliver good incremental recovery in carbonate reservoirs [7]. Current theory is that wettability alteration through surfactant adsorption supplements the effects of mobilization by IFT reduction. Following this thought that would mean that in first approximation a surfactant optimized for IFT reduction under certain reservoir conditions should also perform well in wetting alteration under the same conditions. In a recent work [8] the wettability performance of two series of anionic surfactants, namely alcohol propoxy sulfates with different degrees of propoxylation and alcohol ether carboxylates with defined hydrophilicity ranking, was studied. It was shown that the wettability alteration achievable for a certain reservoir correlates with the surfactant’s hydrophilicity.

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Overall the somewhat more hydrophobic propoxy sulfates showed better results than the ether carboxylates but also within the latter series a trend with hydrophilicity could be observed.

One easy way to measure the effects of additives on wetting behavior is the determination of contact angles. Figure 7 gives a schematic overview. A water drop is placed onto a flat rock surface and the angle at the three phase contact point (surface, liquid, air) is determined. On an oil-wet surface the water droplet keeps its round shape (left) while on a water-wet surface the water droplet can spread completely (right).

**Figure 7** Schematic overview of contact angle measurement.

**Figure 8** Microphotography pictures of an oil-saturated calcite slab in contact with 0.1% alcohol propoxy sulfate in 0.25 mol/l Na2CO₃ solution.
Alternatively with the same measurement setup the desorption of oil droplets from an oil-wet surface in the presence of surfactant solution can be observed directly. Figure 8 shows a series of microphotography pictures: A calcite slab was saturated with crude oil and brought into contact with pure water (not shown) and with a dilute solution of an extended anionic surfactant, an alcohol propoxy sulfate, in sodium carbonate brine. In pure water no desorption at all could be observed. In the surfactant solution it can be seen how the oil at the rock surface desorbs from the surface in a matter of seconds (rising oil droplets). After several minutes new oil droplets form at the calcite surface, indicating the mobilization of oil from within the rock pores.

**Miscible Gas Injection**

Carbon dioxide flooding is a well established technique for enhanced recovery. In times when CO₂ capture and storage is of increasing importance EOR by CO₂ injection becomes even more attractive. The efficiency (or even the possibility) of a CO₂ flood is governed by the miscibility between the CO₂, which is supercritical under most reservoir conditions, and the crude oil.

The highest efficiency is given in so-called first contact miscibility (FCM) conditions: In light crudes the CO₂ is directly and completely miscible with the oil, no separation of heavies or partial extraction occurs. In so-called multiple contact miscibility (MCM) the lighter parts of the oil mix with the CO₂ to form a new equilibrated gas phase while the CO₂ also condenses into the heavier components and mobilizes them by viscosity decrease. In the so formed transition zone this simultaneous vaporization and condensation happens several times, with both phases becoming more similar, until full miscibility is reached. Multiple contact miscibility also leads to increased oil extraction but is less efficient than first contact miscibility because of the potential build up of heavy residues in the reservoir. Crude oils containing mainly heavy components are immiscible with (sc)CO₂; carbon dioxide flooding under immiscible conditions is still possible but considerably less efficient as this process relies mainly on pressure maintenance or increase.

Figure 9 Ternary phase diagrams depicting miscibility behavior of CO₂ with three different oils. Oil composition is given as ratio of lighter and heavier ends.

Figure 9 shows ternary phase diagrams explaining the three possible miscibility states. In case of a crude consisting mainly of light components (“Oil A”) the mixing path between CO₂ and oil passes by the miscibility gap, leading to first contact miscibility (left). In case of “Oil B”, which has more heavy components compared to Oil A, the mixing path crosses the miscibility gap, it comes to multiple phase separations into gas phases and condensed phases with stepwise more similar compositions until finally miscibility is reached (middle). In case of the heaviest “Oil C” the mixing pathway again crosses the miscibility gap. In this case, however, the mixing pathways from the newly generated gas phases always stay in the miscibility gap and can never reach (or cross) the critical point where the compositions of gas phase and condensate phase merge. Therefore this flood will always stay immiscible.
The phase diagrams depicted in Figure 9 are at constant temperature and pressure. It is understood that of course there is also a strong pressure dependency of the miscibility. Increasing the pressure will shrink the miscibility gap. This can shift a former MCM procedure into first contact miscibility or can even make formerly immiscible floods miscible. In practical terms however it is not possible to simply increase the injection pressure of CO2 into a reservoir to make any flood miscible: Higher pressures become more and more uneconomic and the upper possible pressure limit is always given by the fracturing pressure of the formation.

**Figure 10 Reduction of physical minimum miscibility pressure (MMP$_p$) by addition of a chemical additive to CO2.**

We could recently show [9, 10] that suitable additives can reduce the minimum miscibility pressure (MMP) for a given system. Instead of measuring the MMP, defined as the minimum pressure that has to be applied to achieve a miscible procedure, which is a complicated and time consuming procedure, the more accessible physical minimum miscibility pressure (MMP$_p$), the pressure at which complete miscibility is reached, was determined. This can be done by a simple optical observation of the phase state in a pressure resistant sapphire cell. The miscibility of CO$_2$ with a model oil with and without different additives was recorded. It was found that all additives tested were able to reduce the MMP$_p$ to different extents, also depending on the CO$_2$ to oil ratio. Increasing the amount of chemical addition leads to higher pressure reductions [9]. In a subsequent paper this work was extended to a real crude oil and yielded similar results [10].

**Conclusions**

Surfactants and related structures are versatile chemicals that can successfully improve the effectiveness and efficiency of a variety of enhanced oil recovery methods. However, there is no “one size fits all” solution, the requirements for each method are different and should be carefully evaluated before selecting potential candidates for chemical addition. Translating the list of selection criteria in meaningful test methods is the next step. Knowledge of surfactant science fundamentals and access to a good variety of structures helps pre-selecting the right materials to go into testing. Even within one application there is no “best” surfactant for all reservoirs. Performance depends on the best fit of the surfactant structure to the reservoir conditions – compatibility with the oil, right hydrophilicity at the right temperature and physical and chemical stability, just to name a few.
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