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New surfactant developments for chemical enhanced oil recovery

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ABSTRACT

Recent advancements in surfactants for chemical enhanced oil recovery (EOR) are presented. For oils with a high equivalent alkane carbon number (EACN), surfactants with very large hydrophobes are needed to obtain the ultra-low interfacial tensions needed to reduce the residual oil saturation to nearly zero. The need increases at high temperature. Furthermore, these large hydrophobes need to be branched to promote formation of microemulsions with low to moderate viscosity as opposed to gels or other viscous structures that cause high surfactant retention. We show that such surfactants can be made from more than one type of hydrophobe in the form of either alkoxy sulfates or carboxylates. The carboxylates have the advantage of better stability at high temperature. Both the sulfates and carboxylates can be easily tailored to specific reservoir conditions and oils by adjusting the number of ethylene oxide (EO) or propylene oxide (PO) groups in the surfactant. A new correlation has been developed using an extensive data set taking into account the effects of PO number, EO number, temperature, brine salinity and the EACN of the oil on the optimum hydrophobe size. These new developments have enabled us to address a much wider range of conditions of oil characteristics, reservoir temperature, salinity and hardness level. Furthermore, the new surfactants are competitive in cost with previous EOR surfactants. Thus, these new developments have greatly advanced the commercial potential of chemical EOR.

1. Introduction

In general, only approximately one-third of the oil is economically recoverable from the known reserves with the current technology including primary and secondary recovery methods. It has always been the target of petroleum engineers to develop tertiary recovery technology such as chemical EOR to increase overall oil recovery. With the current high oil price, research in EOR, especially surfactant processes, is gaining tremendous interest. With chemical EOR targeting more and more difficult reservoir conditions, conventional surfactants developed in the past few decades show limitations of use in harsh environments and with difficult oils, therefore new high-performance surfactants are highly desirable.

Several classes of new surfactants have recently been synthesized and tested for enhanced oil recovery. These new surfactants were necessary for oil field applications under reservoir conditions that made it difficult or impossible to find conventional surfactants with the desired properties such as ultra-low interfacial tension, aqueous stability, thermal stability at high temperature, low retention, tolerance to high salinity and hardness, and so forth. We illustrate results for several of these new surfactants and discuss under what conditions they are suitable, how we developed chemical formulations using them and some of the general principles that can be applied to future applications. A common theme of this development is the need for surfactants with large hydrophobes (carbon numbers above 18) even for some light oils. A second theme illustrates the advantages and flexibility of propylene oxide and ethylene oxide linkages between these large hydrophobes and the anionic head group (sulfate or carboxylate). A third common theme shows the advantages of highly branched hydrophobes regardless of the other characteristics of the surfactant structure in order to help prevent undesirable viscous phases. Finally, a fourth theme demonstrates the advantages of using surfactant mixtures with diverse structures and sizes. The use of these common elements enable us to find surfactant formulations that are highly effective and that can be made from available chemical feedstocks at a reasonable cost that is competitive with less effective commercial products.

In this paper, we first present the developments of three new classes of large-hydrophobe surfactants including Guerbet alkoxy sulfates, Guerbet alkoxy carboxylates, and Tristyrylphenol alkoxy

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sulfate surfactants in addition to their application under a wide range of reservoir conditions. Next, a new surfactant structure correlation is illustrated that potentially can be used as a guideline for identifying effective surfactant formulations. In addition, a new surfactant retention correlation is presented that can predict retention taking into account the effects of different variables. This correlation could be useful in understanding the impact of each variable on the retention. In the end, we demonstrate the laboratory capability to conduct live oil microemulsion phase behavior experiments using high-pressure sapphire view cells rated to 150 °C and 5000 psi. This allows us to study the impact of solution gas and pressure on microemulsion phase behavior under conditions where almost no data exists, especially at high temperature and pressure conditions.

2. New surfactant developments

2.1. Guerbet alkoxy sulfate (GAS) surfactants

Alkyl alkoxy sulfates with hydrophobes in the range of 12–18 have been used for EOR for many years. Examples can be found in Flaaten et al. (2008) and Levitt et al. (2006). However, their effectiveness decreases as the equivalent alkane carbon number (EACN) of the crude oil increases or as the temperature increases. Many alkyl alkoxy sulfates have very limited branching. Guerbet alcohols (GA) are branched with a relatively high carbon number resulting, making them great surfactant hydrophobes, but they are expensive in a high-purity state. Inexpensive Guerbet alcohols can be prepared by aiming for less than quantitative conversion during the alcohol dimerization process.

The Guerbet reaction dimerizes a linear alcohol using base catalysis at high temperatures (for example 230 °C) to produce near mid-point branching (O'Lenick Jr., 2001). The Guerbet alcohols are considered the "gold" standard for large, branched alcohols which are low melting point liquids. Very large hydrophobe structures can be produced from smaller linear alcohols using the Guerbet reaction. For example, a C32 GA can be produced from a C16 alcohol. These Guerbet alcohols can then be used in the production of corresponding alkoxy sulfate surfactants. Guerbet alkoxy sulfate surfactants have previously been studied at the air–water (Varadaraj et al., 1991) and oil–water interfaces (Aoudia et al., 1995). These anionic surfactants can be produced by adding PO and EO units to the GA, followed by sulfation (O'Lenick Jr. and Parkinson, 1996). By varying the amount of PO and EO in the Guerbet surfactants, they can be tailored to fit specific oil and brine characteristics.

As mentioned previously, the Guerbet alcohols tend to be more expensive than other alcohols when produced in high purity. The high cost is mainly due to driving the reaction to completion and/or stripping-off of the unreacted monomer alcohol to produce high purity. However, inexpensive Guerbet alcohols can be prepared by aiming for less than quantitative conversion during the alcohol dimerization process. The resultant blend of 85–95% GA and 5–15% monomer alcohol is subsequently used in the alkoxylation process to add propylene oxide and/or ethylene oxide, followed by sulfation.

Such mixtures are both less expensive and more effective when made into anionic surfactants for enhanced oil recovery than higher purity GA products that require more reactor time and higher cost to manufacture. The unreacted alcohol monomer subsequently ends up as a co-surfactant during the surfactant manufacturing process with the mixture of surfactants being more effective for EOR than the pure surfactant. Even when higher purity GA are used to produce the alkoxy sulfates, the final surfactant molecules are still of reasonable cost due to the high molecular weight of the sulfate surfactant. For example, in Guerbet C_{32}-7PO-10EO-sulfate the GA is only 33% of the entire surfactant molecule based on weight. Through the use of this new Guerbet process, these surfactants can be manufactured at low cost when made as sulfates as opposed to sulfonates. The use of a GA is a feasible way to produce very large hydrophobe surfactants that can be tailored for particular uses.

One of the limitations of this class of surfactants is their poor hydrolytic stability at temperatures greater than about 60 °C (Talley, 1988). The hydrolysis of ether sulfate (ES) occurs rapidly under acidic conditions. However, under highly basic (very high pH) conditions, base catalyzed hydrolysis of the ES could occur and cause some decomposition of the surfactant. The hydrolysis of ether sulfate surfactants including Guerbet alkoxy sulfates can be vastly reduced over a specific alkalinity range even at high temperatures. The decomposition time in terms of half-life of ether sulfate surfactants is estimated to be about 4–6 years at 85 °C (Adkins et al., 2010).

We have found that this class of surfactants nearly always performs better when mixed with one or more additional surfactants (cosurfactants) with different structures. Cosolvents are sometimes needed as well to provide better aqueous stability or to reduce microemulsion viscosity. The next example illustrates a formulation where both cosurfactants and cosolvents were needed. The cosurfactant in this case is an internal olefin sulfonate (IOS) with a high carbon number. The IOS is a twin tailed surfactant, so it behaves somewhat like a branched surfactant. Both cosurfactants and cosolvents help prevent close packing of surfactant molecules in the micelles, which tends to cause poor transport or high retention in reservoir rocks.

A formulation consisting of 0.25 wt% C_{32}-7PO-14EO-sulfate, 0.25 wt% C_{20-24}-IOS, and 0.5 wt% TEGBE cosolvent was tested at 100 °C. The oil used for this formulation is a light oil (API=29, μ_o=4.0 cp) with a low acid number (i.e. oil is inactive). The microemulsion phase behavior using this surfactant formulation is shown in Fig. 1. The solubilization ratio at the optimal salinity is about 17 corresponding to an ultra-low IFT of 1.0×10^{-3} dyn/cm. The aqueous solution including 500 ppm Flopaam 3630 s polymer is clear and stable at 100 °C up to 35,000 ppm sodium carbonate.

A coreflood experiment was performed in Bentheimer sandstone to evaluate the performance of this surfactant formulation. The Bentheimer sandstone used in this coreflood had a permeability of 2500 md and a porosity of 0.217. A 0.5 pore volume (PV) surfactant slug with 0.5 wt% formulation concentration (C) was injected followed by a polymer drive. The oil recovery was 94.7% of the residual oil saturation after waterflood and the final oil saturation was about 0.02 (Fig. 2). The surfactant retention was

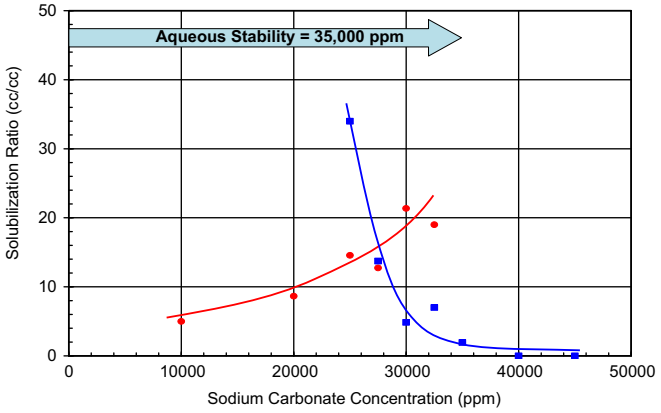

Fig. 1. Phase behavior of 0.25 wt% C_{32}-7PO-14EO-sulfate, 0.25 wt% C_{20-24}-IOS, and 0.5 wt% TEGBE at 100 °C with 50 vol% oil after 115 days.