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Technical Bulletin

Surfactants for Enhanced Oil Recovery - Thermal Stability and Ionic Tolerance

Huntsman is a global supplier of surfactants and other chemicals widely used in oilfield operations. Included are Enhanced Oil Recovery (EOR) surfactants designed to meet the challenges of varying reservoir, injection water, and crude oil properties.

An effective EOR formulation requires the surfactant component to be stable to conditions within the target reservoir formation. This includes being both thermally stable and compatible with the injection water.

Thermal Stability

Surfactants selected for use in an EOR flood must have a molecular structure that will allow them to be thermally stable for the duration of flood. Most EOR surfactants are anionic sulfonates or sulfates. The ether sulfates have the anionic $-SO_3Na$ group attached to a propylene oxide (PO) or ethylene oxide (EO) group, while in sulfonates, the $-SO_3Na$ group is attached directly to a carbon in the alkyl or alkylaryl structure. In general, the thermal stability of an anionic surfactant follows in order of increasing stability:

$$EO\text{-}SO_3Na < PO\text{-}SO_3Na < Ether\ C\text{-}SO_3Na < Alkyl\ or\ Alkylaryl\ Sulfonates$$

(Ethoxy Sulfates) (Propoxy Sulfates) (Ether Sulfonates) (Alkyl or Alkylarl Sulfonates)

Other factors such as injection water quality and pH will also affect thermal stability. Pope, et.al. recently reported that the stability of ether sulfates was greatly improved by maintaining the pH between 10 and 11.

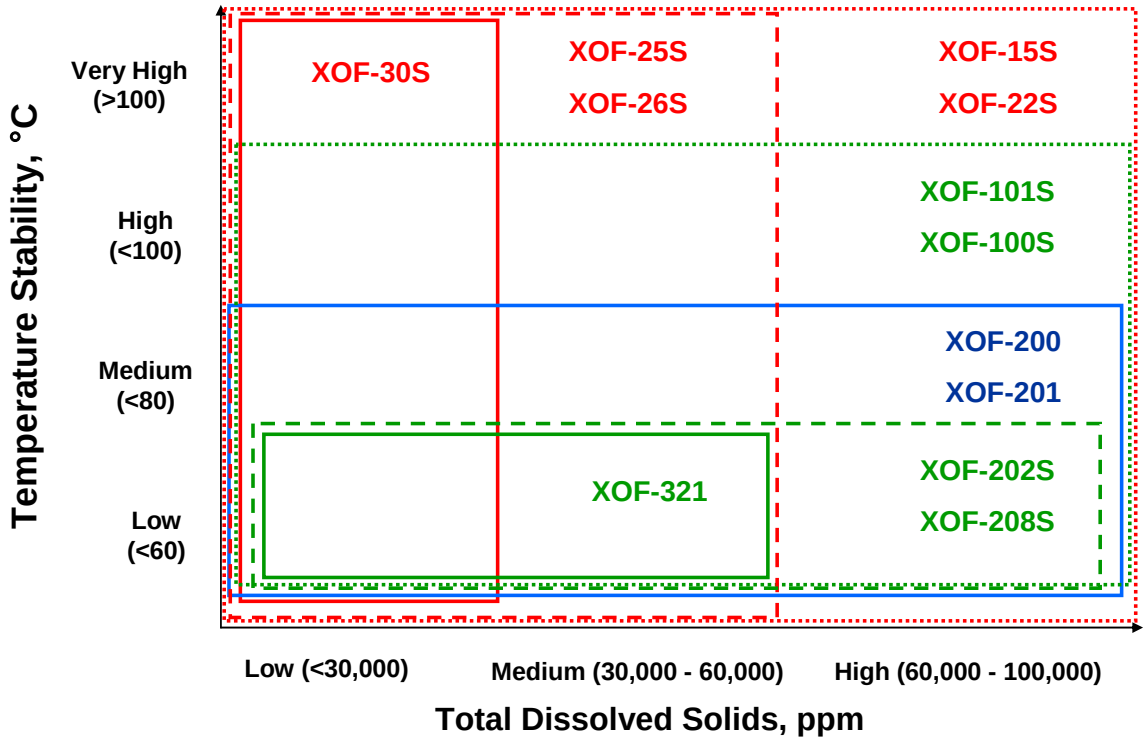
As shown in Table 1, Huntsman has a variety of surfactants with molecular structures that are useful from moderately warm (60°C or less) to very high (>100°C) temperature reservoirs.

Table 1
Huntsman Surfactants for EOR

Product Name	Product Description
XOF-100S	Branched Alcohol + xPO, sulfated, Na salt (Low MW)
XOF-101S	Branched Alcohol + xPO, sulfated, Na salt (Medium MW)
XOF-200	Sulfosuccinate, Low Flash Point
XOF-201	Sulfosuccinate, High Flash Point
XOF-202S	Linear Alcohol + xPO + yEO, sulfated, Na salt (Med MW)
XOF-208S	Linear Alcohol + xPO + yEO, sulfated, Na salt (High MW)
XOF-15S	Alkylaryl Sulfonate (Low MW)
XOF-22S	Alkylaryl Sulfonate (Low-Medium MW)
XOF-25S	Alkylaryl Sulfonate (Medium MW)
XOF-26S	Alkylaryl Sulfonate (Medium-High MW)
XOF-30S	Alkylaryl Sulfonate (High MW)
XOF-321	Blend of an ether sulfate and an alkylaryl sulfonate

The vertical axis of Figure 1 shows the recommended temperature ranges for each of the Huntsman EOR surfactants.

Figure 1
Thermal Usage Range



The surfactants XOF-200 and XOF-201 are special in that their sulfosuccinate structures degrade not at the C-SO_3Na location, but where the amyl alcohols attach. At temperatures higher than 80°C, the alcohols hydrolyze and become co-solvents. For high temperature applications, these molecules have become known as “sacrificial surfactants” because they stabilize the EOR package only long enough for the package to be injected. At temperatures lower than 80°C, these sulfosuccinates are known as “universal co-solvents” because they can stabilize an EOR package to high amounts of Total Dissolved Solids (TDS).

Ionic Stability

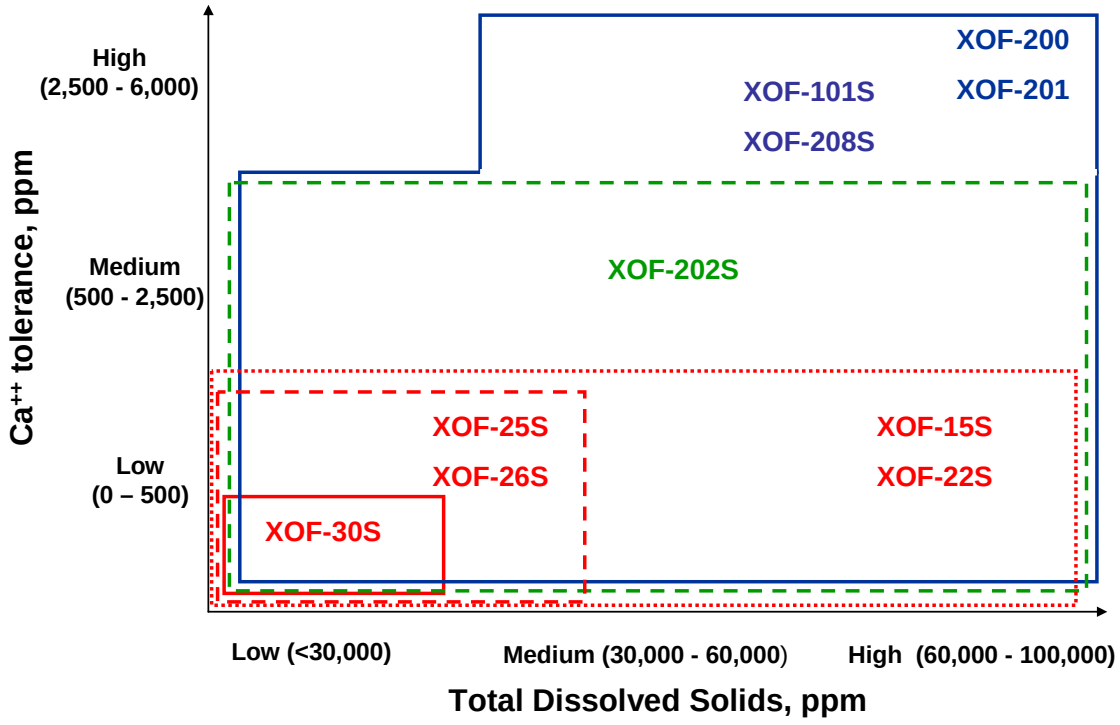
Successful application of an EOR surfactant package requires the formulation to be compatible with the injection water. The injection water is usually described by Total Dissolved Solids (TDS) and its components – salinity and hardness.

Just like molecular structure can affect thermal stability, it can also affect tolerance to electrolytes. In general, ether sulfates are more tolerant of salinity than alkylaryl sulfonates. The molecular weight of the hydrophobe also plays a key role, with small hydrophobes being much more soluble. For example, XOF-15S will be more soluble than XOF-30S because of the different size of the hydrophobic components in the two products.

The term “hardness” is used to describe the presence of divalent ions, i.e., Ca^{++} and Mg^{++}, in solution. Alcohol ether sulfates typically are much more tolerant to water hardness than alkylaryl sulfonates. Hard water tolerance is also improved by the presence of ethylene oxide units in the surfactant molecule. Incorporating the EO into the anionic surfactant is better than adding a nonionic surfactant to the formulation because cloud point and chromatography effects are avoided.

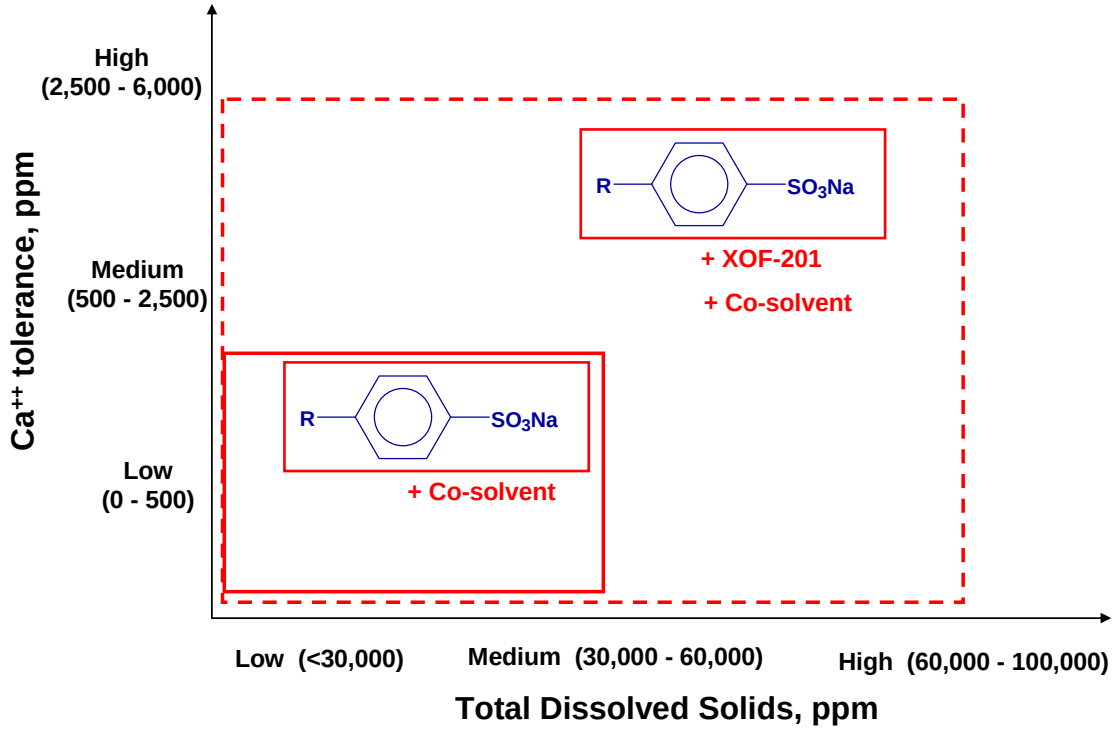
The vertical axis of Figure 2 shows the recommended water hardness ranges for each of the Huntsman EOR surfactants.

Figure 2
Total Dissolved Solids Usage Range



For alkylaryl sulfonates, the hardness tolerance remains relatively low regardless of molecular weight. As shown in Figure 3, these surfactants must be blended with co-solvents and co-surfactants in order to expand their useful TDS and hardness range. In applications that involve reservoir temperatures less than 80°C, the sulfosuccinate co-surfactants XOF-200 and XOF-201 work very well.

Figure 3
Extension of Total Dissolved Solids Usage Range



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