- **TITLE**: Tuneable Task – Specific Surfactants for EOR under Different Salinity Ranges
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- **ABSTRACT**

Nowadays, the demand of crude oil continuously increases. However, the findings of crude oil reservoirs are limited, and it becomes necessary to improve the oil production in the already known reservoirs. Chemical EOR has been shown as an effective alternative to meet this necessity. Nonetheless, the current economic situation worldwide and the decreasing trend of crude oil prices requires new processes and/or chemicals that could make the economic viability of EOR projects feasible.

In this work, the influence of two key sulfonation parameters (free oil and free sulfuric acid contents) on the compatibility and brine tolerance is shown. This could make LAS (Linear Alkylbenzene Sulfonate) surfactants versatile for different EOR projects, reducing the research, inversion in facilities and production costs, and conferring economic viability to the chemical EOR. Moreover, by selecting a suitable catalyst for production of the precursor, LAS with higher viscosity can be obtained. The polymer concentration (if used) of the final formulation would be reduced or eliminated, improving once more the economics of the process.

TITTLE: TUNEABLE TASK-SPECIFIC SURFACTANTS FOR EOR UNDER DIFFERENT SALINITY RANGES

- ## Introduction

Green alternative technologies are thought to meet future energetic demand while reducing dependence on the fossil fuels that currently drive the planet's economies. Even when these renewable technologies (such as biofuels, biomass, solar energy, tidal power, wind power, geothermal, etc) are being deeply studied, the dependence of humankind on fossil energy is still too strong. Among the different options, crude oil is the most used energetic source, being transportation and refineries the main responsible for this high consumption [1]. Moreover, as it can be seen in Figure 1, the International Energy Agency forecasts a growing trend for the oil demand, and the consumption seems to increase in the next years [2].

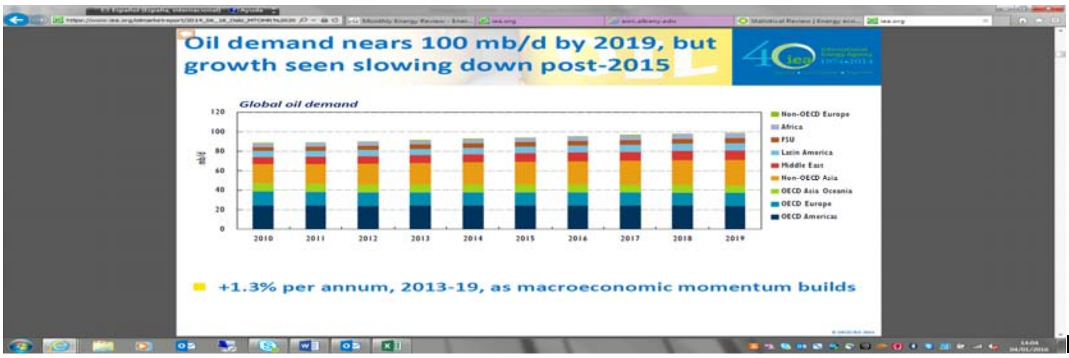

Figure 1. International Energy Agency forecast on global oil demand

Due to this huge consumption and to the fact that the findings of crude oil reservoirs are limited, it becomes necessary to improve the oil production in the already known reservoirs. Oil fields are firstly exploited by natural pressure difference: it means that the pressure gradient between the reservoir and the surface makes the oil come to the surface. In this step (primary recovery), a 5-15% of the oil in place is recovered. Then, once the natural gradient pressure is not effective anymore, secondary recovery is carried out by means of external injecting fluids that will supply external energy to the reservoir, increasing its internal pressures and making, thus, the oil recovery possible. The most common fluids used in this stage are mainly water, natural gas, CO_2, or air. After this step, a 35-45% of the original oil in place is recovered.

Since up to two thirds of the crude oil remains in the reservoirs after primary and secondary recovery [3], tertiary oil recovery or enhanced oil recovery (EOR) is required to optimize the economy of the extraction, as the remaining oil is trapped in the pore structure of the reservoir. From a fundamental point of view EOR should be understood as a combination of techniques or methods that will add extrinsic energy and materials to a reservoir in order to control the wettability of the rock and the interfacial tension (oil-water, as well as to move the remaining crude oil in a controlled manner to a production well [4]).

EOR can be carried out by using different techniques [5-8]:

- Mobility control, where favorable mobility ratios are maintained between crude oil and water. With this aim, the viscosity of the water phase is increased.
- Miscible processes, in which the injection of a gas or a fluid oil-miscible at reservoir conditions mobilize the crude oil.
- Thermal processes, that rely on the use of thermal energy, namely steam, hot water or combustible gas. The increase in the temperature of the trapped oil leads to a decrease in its viscosity, and a better mobility thus.
- Microbial. This method manipulates the microbial environment of the oil reservoir.
- Chemical, where specific chemicals are injected to create desirable phase behavior properties, in order to improve oil displacement.

Moreover, several processes can be combined, taking advantage of the performance of each selected method for different steps of the EOR process.

Nonetheless, and because waterflooding was already applied to most of oil fields, chemical EOR can be used with less additional facilities requirements [9]. A common chemical process is surfactant flooding. The use of surfactants for oil recovery has been well studied for over 80 years. Water-soluble surfactants were described as an aid to improve oil recovery in fields [10]. This process attempts to reduce the capillary forces restraining the oil and alter viscosity of the displacing fluid in order to modify the viscous forces being applied to drive oil out of the pores. The ratio of viscous forces to capillary forces actually correlates well with the residual oil saturation and is termed the capillary number as follows:

[Eq. 1]

Where μ and V are the viscosity and Darcy velocity of the displacing fluid, γ is the interfacial tension, IFT, and   is the porosity. Higher N_c implies a smaller capillary trapping force, and therefore results in higher recovery. Additional oil recovery requires increasing the capillary number at least several orders of magnitude. This can be achieved by increasing the viscous forces, but practical limitations on the size of pumps and the aim of avoiding fractures in the reservoir make this option unfeasible. However, by adding a suitable surfactant to the water the interfacial tension can be decreased to an ultralow level (~10^{-3} mN/m), which enables the recovery of oil from much smaller pores and improves displacement efficiency. This phenomenon forms the basis for surfactant-based chemical EOR processes. Then, an effective way to determine the recovery performance of a chemical EOR consists on measuring the IFT between the designed formulation and the crude oil. The lower the value, the easier the crude oil will be displaced by the formulation.

By combining this reduction with the mobility control of the phase (by polymer addition), a surfactant-polymer technique, SP, takes place, making the process more robust and suitable for a wider range of conditions. Although this method has a great potential, it means higher costs. It is desirable to design the most efficient process with the aim of increase the oil recovery, but economic feasibility of the EOR process is more critical than any other factor.

However, current economic scenario makes the EOR projects less viable. Figure 2 shows the International Energy Agency data with the oil price trend during 2015. Furthermore, forecasts point out a standstill or a slow increase in prices for the next months.

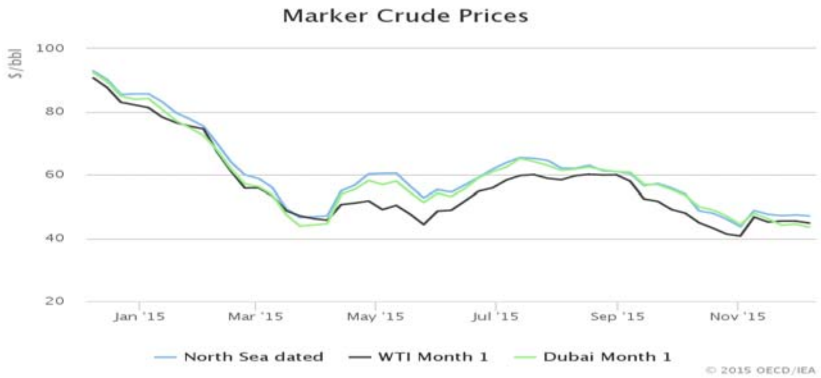

Figure 2. Marker crude prices in the last year

Taking this into account, and to make the SP EOR process viable, it would be necessary to reduce costs by using cheaper chemicals (or even simpler formulations). However, EOR projects are often expensive, due not only to the price of the used chemicals but also to the research stage. The obtaining of a suitable formulation for a specific reservoir may take several months or even years of experimental work. Furthermore, when a new reservoir with different conditions is studied neither the complex formulation of chemicals nor the facilities used in previous fields are guaranteed to be similar. This supposes an expensive and time-consuming stage in the EOR projects. Thus, a proper research workflow will be defined depending on the specific reservoir conditions, such us:

- Temperature: High, medium or low.
- Brine salinity: Monovalent and Divalent cations.
- Crude Oil: Alkane Equivalent Number (EACN), API, and Composition (SARA).
- Type of Rock: high, medium or low adsorption.

Thinking of an integrated process, where surfactants are produced and then used in SP formulations for EOR, the necessity of producing specific surfactants as a function of the target reservoir makes the feasibility of the project harder, too.

To overcome all this drawbacks, the production of a more versatile surfactant (suitable for a wide range of salinity conditions) is presented in this work. A versatile product would not only reduce manufacturing and facilities costs but also time and cost of the previous researching step. Furthermore, if the viscosity of the surfactant could be tuned for the different requirements, savings in polymers would also be achieved. With that aim, the industrial manufacture of a surfactant that could change its applicability range in EOR project by just adjusting some operational conditions in its production is suggested.

• Linear Alkylbenzene Sulfonate (LAS)

Linear Alkylbenzene Sulfonate (LAS) is the most widely used surfactant world-wide, present in almost all type of finished products either for household use or industrial and institutional applications. Besides its performance as tensioactive agent, LAS is fully biodegradable by both aerobic and anaerobic pathways.

It is formed, as it can be seen in Figure 3, by a linear alkyl chain with a benzene ring. This ring has a neutralized sulfonate in position *para* respect to the hydrocarbon chain.

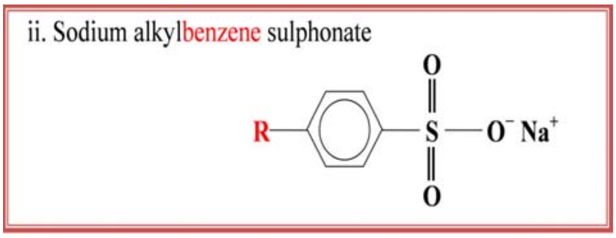

Figure 3. Example of LAS: Sodium 5-alkylbenzene sulfonate

LAS is obtained by the neutralization of the corresponding linear alkylbenzenesulfonic acid (HLAS), which is produced by sulfonating a linear alkylbenzene (LAB).

- ## Sulfonation process. Influence of parameters

More than 98% of the LAB produced world-wide is converted into the corresponding sulfonic acid by sulfonation. This reaction consists in mixing sulfur trioxide (SO_3) with the organic feed (LAB). The sulfonation process must be carefully controlled, paying attention to the following operating parameters [11,12]:

- Temperature: The sulfonation is exotermic and therefore all commercial reactors are provided with a cooling system to keep the sulfonation temperature in the range of 40-50ºC and minimize the color undesirable effects.
- SO_3/LAB molar ratio: The SO_3/LAB molar ratio is a key parameter for the completeness of the reaction as well as for the quality of the sulfonic acid. Sulfonation reaction takes place on a mol mol basis, although on a commercial scale it is nearly impossible to reach a stoichiometric ratio of reactants, due to other competing side reactions, which unavoidably take place. Consequently, SO_3 is always in excess over LAB. The excess will be transformed into H_2SO_4 during the final step of the sulfonation process.

Depending on the reaction conditions, the quality of the final product can be substantially different, even when the starting raw material is the same. When the sulfonation is completed, the product (sulfonic acid) is analyzed to control the quality parameters: active matter content (AM), unsulfonated matter or free oil (FO), free sulfuric acid, acidity index (AI), and water content. The control of the sulfonation variables will determine the characteristics and the applications of the final product.

Once the HLAS is produced, the final LAS is obtained by direct neutralization, usually with sodium hydroxide.

- ## Surfactants in EOR

Surfactants are the main ingredient of many chemical EOR formulations. They can be prepared by mixing different surfactants, adding solubility improvement agents (namely alcohols), polymers, alkali, etc. Nonetheless, there are some requirements to make the formulation suitable for that purpose:

IFT performance

The use of surfactants in EOR processes is determined by physico-chemical requirements. First of all, the surfactant used in the formulation must ensure the compatibility with the other components, and be soluble under the target salinity of the well (salinity tolerance). Despite the surfactant is usually present in chemical EOR formulations in low concentrations, it is the main ingredient. Thus, the more viscous it is the more improved the mobility control will be.

With the aim of evaluating a surfactant as candidate for an EOR formulation a combination of different tests have to be carried out: study of the phase behavior by means of Winsor diagrams, adsorption on reservoir rocks, determination of the critical micelle concentration, thermal stability, coreflooding experiments… But, probably, the most important test, and the one that provides the most direct and easiest information on its performance is the evaluation of the IFT. For that purpose, the designed formulation is put in contact with a sample of the reservoir oil under different salinity conditions, and the value of interfacial tension is measured when equilibrium is reached among both phases. The formulation (surfactant) can be then tuned to obtain a minimum IFT value at the target salinity.

Compatibility

One of the main problems of the chemical EOR is the mobility control of the formulation inside the well. When the connections between the porous of the rocks are low, it is necessary to introduce a polymer in the formulation to increase the sweep efficiency and to avoid the preferred channel. However, the inclusion of polymer in the formulation could affect the stability of the formulation, giving place to precipitation of the surfactant or phase separation. A precipitation of the phase inside the well could plug the porous and triggering an overpressure.

So, the designed formulation must accomplish compatibility requirements of the surfactant with the polymer (if used) in order to avoid the aforementioned precipitation phenomena.

Solubility / salinity tolerance

The free sulfuric acid present in the surfactant is formed by excess of SO_3 used in the sulfonation reaction. As it was mentioned before, the ratio SO_3/LAB is one of the key parameters during the reaction. The sulfuric acid improves the solubility of the surfactant. Thus, adjusting the percentage present in the sample, the surfactant could be used for fields with harsh reservoir conditions (with high salinity).

Nowadays, the surfactants are classified according to their use in fields of high, medium or low salinity brine. The type of surfactant, the structure, the chain, the hydrophilic and hydrophobic groups are different depending on the application field, and, then, the manufacture process could need to suffer modifications in order to adjust the product to the salinity water of injection (brine).

- ### Viscosity

The viscosity is an important parameter to consider in a final formulation. The mobility control inside of the porous media is fundamental to improve the recovery factor of oil. As a general rule, the viscosity of the formulation is provided by the polymer. However, it must be taken into account that the inclusion of a new component increases the price of the formulation and makes the process less profitable.

- ## On the design of a task-specific surfactant for EOR: results

- ### Free oil

The compatibility between surfactant – polymer can be improved by adjusting the percentage of free oil of the final product. The unsulfonated matter is composed by oil-based products, which lubricate the interaction between the chains of surfactant and polymers. It provides stability to the formulation over time.

On other hand, the percentage of free oil of the surfactant can aid to adjust the formulation to the optimal point. The formulations for surfactant EOR are designed for an exactly amount of salts present in the brine water. Changes in the monovalent or divalent cations may affect the oil or water affinity and the interfacial tension of the dissolution, turning it ineffective for enhanced oil recovery. Nonetheless, the free oil of the surfactant can solve the problem. A higher amount of unsulfonated matter confers to the formulation better interaction with the crude oil. Figure 4 shows the improvement in compatibility of a formulation by modifying the free oil of the surfactant.

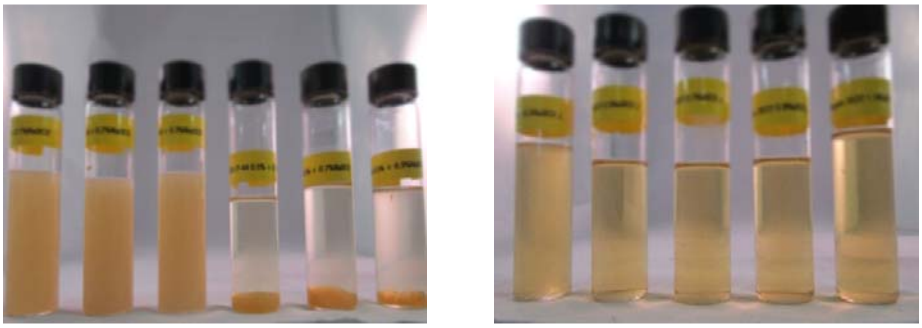

Figure 4. Improvement of compatibility of an EOR formulation under a range of salinities by optimizing the FO content (left: before optimization, right: optimized FO)

- ## Free sulfuric acid content

As previously explained, with the optimization of the sulfuric acid content, the same surfactant might be used for fields of different salinities and characteristics, making it a feasible option for different EOR projects. The influence of the sulfuric content on the IFT performance of a LAS surfactant is showed in Figure 5. It can be observed that soft (and simple) variations in the operational parameters of the sulfonation step can lead to the obtaining of a versatile surfactant suitable for different salinity scenarios.

Figure 5. Influence of the H_2SO_4 content on the IFT performance of a LAS surfactant

- ## Viscosity modification

The use of a suitable catalyst in the obtaining of the LAB can increase the viscosity of the final surfactant. This improvement could be used to reach the target viscosity of the designed formulation by reducing (or even avoiding) the use of polymer, what means an important save in the final formulation.

The influence of the catalyst used during the LAB manufacture on the viscosity of the final LAS (as well as in the final formulation) is shown in Figures 6 and 7, respectively. It can be seen that a remarkable increase in the viscosity of both surfactant and formulation is obtained for different LAS-type surfactants and different formulations when using an optimized catalyst (CAT B), in comparison with a classical one (CAT A).

Figure 6. Influence of the catalyst used in the alkylation step on the viscosity value, for two different LAS

Figure 7. Influence of a modified LAS on final formulation viscosity, for three different formulations

Conclusions

High demand of crude oil is required worldwide nowadays. However, the findings of crude oil reservoirs are limited, and it becomes necessary to improve the oil production in the already known reservoirs. Since up to two thirds of the crude oil remains in the reservoirs after primary and secondary recovery processes, tertiary oil recovery or enhanced oil recovery (EOR) is required to optimize the economy of the extraction. A common chemical process is surfactant flooding, where a surfactant is used to reduce the oil-water interfacial tension and make the chemical formulation penetrate more easily within the small pores of the reservoirs, releasing more oil.

However, current economic scenario makes the EOR projects less viable. It is necessary to reduce costs by using cheaper chemicals (or even simpler formulations), as well as decreasing the research stage time. To overcome all this drawbacks, the production of a more versatile surfactant (suitable for a wide range of salinity conditions and different fields) is presented in this work.

Linear Alkylbenzene Sulfonate (LAS) is the most widely used surfactant world-wide, and it is produced by sulfonating a linear alkylbenzene (LAB), with a subsequent neutralization of the acid. Depending on the sulfonation conditions, the quality of the final product can be substantially different, and its performance on EOR formulations can be tuned attending to the operational parameters of the reaction. Compatibility within the formulation, resistance to salinity, low IFT values and suitable viscosity are desired conditions for a surfactant in order to be satisfactorily used in a chemical EOR project.

In this work, the influence of the compatibility of a LAS-based formulation depending on the free oil content is presented, pointing out that a judicious selection of the sulfonation parameters can strongly improve the compatibility of the surfactant in the formulation. Moreover, by a simple modification in the sulfuric acid content of the LAS, the same surfactant can be used for a wide range of salinity fields. This would make the surfactant versatile for different EOR projects, reducing the research, inversion in facilities and production costs, and conferring economic viability to the chemical EOR.

Finally, by properly selecting the catalyst for the LAB production, LAS with higher viscosity can be obtained. The polymer concentration (if used) of the final formulation would be reduced or eliminated, improving once more the economics of the process.

Further studies beyond this work, considering economic evaluation and life cycle analysis of the whole process, would be required to conclude about the real impact of these improvements.

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