

## Experimental study of the composition of LAS surfactant mixtures for EOR use

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### Abstract

There is an expected increase in energy demand in the near future, which can indicate that the fossil fuels consumption will also increase at a high rate. This will lead to the necessity to increase the yield of crude extraction to its maximum, which will create investment in enhanced oil recovery (EOR) processes.

This study was made in the chemical EOR extraction area, for processes that use surfactants and polymer. These processes are influenced by numerous factors. This work was focused in the changes in interfacial tension, in viscosity and in the compatibility between the polymer and surfactant. The used polymer was partially hydrolyzed polyacrylamide (HPAM) and the surfactant was a linear alkylbenzene sulphonate (LAS).

Besides the surfactant being studied the surfactant mixtures included Free Oil (FO), which is the unconverted raw material, water and sulfuric acid (when the mixture is the acid forma) or sodium sulphate (when the mixture is neutralized).

The influence of the surfactant mixtures' concentration of sulphate and FO in the mentioned factors was studied. It wasn't detected any connection between the sulphate concentration increase and the studied parameters. On the other hand, an increase in the FO concentration improves substantially the compatibility between the polymer and the surfactant. The interfacial tension measured for the aqueous solutions of surfactant was increased when the FO percentage in the mixture was larger. This is an unwanted effect because it leads to a reduction of the yield of crude extraction. For this reason the FO concentration should be controlled when using surfactants in EOR.

Keywords: Surfactant, LAS, EOR, interfacial tension, FO, sodium sulphate

### 1. Introduction

The world is dependent of the energy supply. All our daily tasks use devices that consume energy.

Given the population growth that has been observed, it is predicted that until 2040, the energy demand will increase 35% [1]. Although it's predicted that the use of oil will decrease in many consumption areas, it will keep its importance in the transportation area. The increasing world population and the development of emergent economies will lead to a growth in the number of light duty vehicles, from 800 million, in 2010, to 1,7 billion, in 2040 [1]. These data suggest that the demand of automobile fuels will increase, creating the increase of oil consumption in this area.

It was predicted that by 2040, about 65 percent of the world's recoverable crude and condensate resource base will have yet to be produced. [1]. Even as global oil production rises, the estimated size of the global recoverable resource base continues to increase as a result of advancements in science and technology that have enabled the production of new sources of liquid fuels.

### 1.1. Crude extraction

There are three possible stages in crude extraction.

A primary phase occurs by pressure drive, given the fact that the pressure inside the well is larger than the atmospheric pressure. On average it is possible to extract approximately 10 to 15% of the existing oil in the well using this method, which takes place until the moment when the pressure inside the reserve is the same as the outside.

In the secondary recovery a fluid less expensive than oil, usually water or natural gas, is injected into the reservoir to maintain the pressure gradient. These fluids are injected into an injector well and drag a portion of the oil to the producing wells or extractors. This phase of recovery allows the extraction of about 30% of the oil inside the reservoir. The third phase of recovery is also known as Enhanced Oil Recovery (EOR). These methods are divided in three groups: thermal methods, chemical injection and gas injection. This extraction step allows the recovery from 50 to 80% of the crude oil existent in the reservoir.

The present work is focuses in the surfactants used in the extraction of crude oil using chemical methods, more specifically the injection of a solution combining surfactant, polymer and an alkaline solution.

### 1.2. Surfactants

Surfactants are molecules which have a polar (hydrophilic) head and an apolar (hydrophobic) tail. This characteristic allows the interaction of these molecules with the interface between two phases with different polarities, by the reduction of the interfacial tension between them.

The hydrophobic part is usually made by a hydrocarbon chain which may be linear or ramified, saturated or not, and can have one or more groups that give different properties to the surfactant.

Surfactants can be classified in two main groups: ionic or non-ionic, based on the constitution of its polar head. The ionic surfactants can be anionic, cationic or amphoteric. The anionic surfactants are divided by families depending on the constitution of the functional group present in the polar part of the molecule. Some of those families are sulfonate, sulfate, fosfate and carboxylate. The surfactant used in this work is a linear alkylbenzene sulfonate (LAS).



Figure 1 – Representation of the LAS molecule.

Surfactants have two important properties shortly described ahead.

## 1.3. Critical micelar concentration

When diluted in aqueous solution the surfactant monomers will be located at the interface with the hydrophilic part directed into the medium and the hydrophobic chain being repelled by the aqueous solution. As the concentration increases, the interface will continue to be populated until it is saturated. At this point (CMC), the surfactant monomers diluted in the solution start to form a lower energy conformation, i.e. protecting its hydrophobic chains with other monomers, forming a micelle. These structures are responsible for the solubilization of the residual oil. Until this point, the interfacial tension (IFT) decreases with the increase in the concentration of surfactant. From CMC on the IFT will be kept constant.

## 1.4. Krafft temperature

In the dissolution of surfactants (ionic) there is a minimum temperature ( $T_{krafft}$ ) and concentration (CMC) needed for the formation of the first micelle. In this point, the solubility of the surfactant increases exponentially because the solubility transitions from molecular to micelar.

### 1.5. Interfacial tension

The interfacial tension (IFT) is caracterized by the interaction of two contacting fases. It can be defined as the free Gibbs energy by area unit and it's usually expressed in mN/m.

The capacity of a surfactant to lower the IFT is a critical parameter in an EOR process. The point where the IFT is minimal represents the optimum formulation and indicates the performance of the surfactant to solubilize the crude oil in the reservoir.

The IFT can be measured many ways; in this work it was measured using a spinning drop tensiometer. This equipment has a horizontal capillary which is filled with the surfactant solution, where a drop of crude oil is injected. Then the capillary is submitted to a rotation movement (between 2000 rpm and 6000 rpm) that leads to the drop deformation, making it longer.





The following equation indicates the relation between the drop radius and the IFT value.

$$IFT = rac{r^3 \Delta 
ho \omega^2}{4}$$
 (1)

To validate a measurement in this tensiometer the length of the drop has to be higher than 4 times its Daymeter.

### 1.6. Hydrophilic-Lipophilic Deviation (HLD)

The HLD is a dimensionless empirical correlation that indicates the deviation to the optimum formulation. The general formula of the HLD method is:

### $HLD = \sigma + \ln sal - kEACN + t\Delta T + aA$ (2)

HLD takes into account the salinity of the aqueous medium (sal), the type of surfactant (k), the hydrophobicity of the organic phase (EACN), the influence of the addition of alcohol (A) and its concentration (a), a characteristic parameter of the surfactant ( $\sigma$ ), and system temperature (t and  $\Delta$ T).

An optimal formulation translates into HLD equal to 0.

### **1.7.** Winsor classification

According to Winsor a ternary system with surfactant, water and oil can be arranged in three different ways.



## Figure 3 – Winsor classification of solution behaviour [23].

Two phases, where one is a micro emulsion phase in equilibrium with one organic phase (R<1; Winsor I); two phases where the micro emulsion is in equilibrium with one water phase (R>1; Winsor II); Tree phases, where one micro emulsion phase in equilibrium with one organic and one water phase (R=1; Winsor III). This last state is called optimum formulation.

The optimum formulation occurs when there is an equal volume of solubilized water and oil (for a determined surfactant concentration) in form of a microemulsion. In this state, the system presents a minimum IFT.

### 2. Experimental Methods

This work required some laboratorial work based on a number of techniques.

### 2.1. Neutralization

The raw material of all the studies was the surfactant mixture. These mixtures could be in acid or neutralized form. If the sample was acid it was necessary to neutralize the sample with sodium hydroxide. There is a significant increase in the sample viscosity, so it is necessary to watch over the recipient during the mixing time. The NaOH is added to the mixture in parts and the pH should be measured until it is found to be between 7 and 9.

# 2.2. Determination of the mixtures' compositions

The surfactant mixtures have, besides surfactant, free oil which is the raw material that didn't react in the sulfonation step of the producing process; water; and sulfuric acid if the mixture is in acid form, or sodium sulfate, it the mixture is in its neutralized form.

# 2.3. Preparation of the compatibility solutions

The compatibility solutions can also be known as formulations. This means that these are the solutions that are being tested in order to choose the best sample to use in an injection of these components in a reservoir. A compatibility solution is constituted by surfactant mixture, polymer, salted water from the reservoir, auxiliary surfactant and a solution of sodium carbonate.

The preparation of these solutions is divided by steps and occurs at 60°C. First the polymer is weighted in the beaker and put in the heating plate, being heated during 5 min. Then a solution of the surfactant mixture and the auxiliary surfactant is added and the solution is mixed and heated for 10 min. Next the salt water is added, mixed and heated for another 10 min. Finally, occurs the addition of the sodium carbonate solution. The compatibility solution stays in the heating plate for another 10 min being mixed. After the preparation this solution is introduced in small test tubes, and a larger one is filled with what is left over. This larger amount is then used to measure the main parameters. The smaller tubes are introduced in hot ovens at three temperatures  $40^{\circ}$ C,  $60^{\circ}$ C and  $80^{\circ}$ C.

### 2.4. Quantitative evaluation of properties

The quantitative evaluation of properties is done using mostly the compatibility solutions, except the measurements of interfacial tension that use both types of solutions.

To measure the interfacial tension a spinning drop tensiometer is used and the hydrocarbon chosen was crude oil. The equipment and the crude oil characteristics are presented in Annex.

To measure the transmittance, the smaller test tubes are used in the colorimeter.

To measure viscosity, it is used a concentric tubes viscosimeter, with a bath at  $40^{\circ}$ C, at different rotation velocities.

### 2.5. Qualitative evaluation of properties

The qualitative evaluation of the mixtures is divided in the solubility study and in the compatibility study. The solubility study is done at room temperature with aqueous solutions, and the compatibility study uses the compatibility solutions at is done at 40°C, 60°C and 80°C. Both properties are evaluated through observation throughout the time of the study. If the sample precipitates early it indicates that it has low compatibility or solubility, depending on the solution being analyzed.

### 3. Results and Discussion

This work is divided in three studies: the influence of sulfate and free oil, and the study with an industrial sample. The main objective of this work was to analyze the influence of alterations in the composition of the surfactant mixtures in the compatibility between surfactant and polymer. In every study the same parameters were evaluated: Interfacial tension, viscosity, compatibility and transmittance. In this article, only the main results are presented.

### 3.1. Sulfate study

In this study the objective was to confirm if the sulfuric acid concentration had influence in the evaluated parameters. In the next table it is possible to observe the compositions of the samples used in this study.

Table	e 1 - (	Compositio	on o	f the	used	samples	in	the
study	of the	e influence	of s	ulfate	e.			

Samples:	С	C1	C2	C3	C-a	C-b
			Acid			
MA (%)	77,80	77,50	77,02	76,03	73,48	76,26
FO (%)	19,00	19,00	18,98	18,97	20,31	18,99
H₂SO₄ (%)	3,10	3,50	4,00	5,00	6,21	4,75
H₂O (%)	0,10	0,00	0,00	0,00	0,00	0,00
		Neu	tralized			
MA (%)	60,20	60,18	60,16	60,11	60,95	60,12
FO (%)	14,70	14,70	14,69	14,68	15,02	14,23
Na₂SO₄ (%)	3,47	3,92	4,48	5,60	7,13	5,18
H₂O (%)	21,63	21,20	20,67	19,61	16,90	20,47

When the viscosity was measured there was an unexpected observation: an increase in sulfate/sulfuric acid concentration led to a significant increase in viscosity, visible in figure 4. Although being unexpected this effect is positive due to the fact that viscosity is one of the main parameters that influence the efficiency of chemical EOR projects.





In the next table is represented the state of the compatibility solutions in three points in time. In the table, green represents solutions in good state, in yellow solutions that show the beginning of precipitation, and in red precipitated solutions. It is noticeable that there was no correlation between the sulfate concentration and the precipitation of the solutions.

Table 2 – Evolution of the compatibility solutions.

40°C	[	Day 1	5	[	Day 30	)	Day 45					
40 C	0,3	0,5	0,7	0,3	0,5	0,7	0,3	0,5	0,7			
С												
C1												
C2												
C3												

In this study wasn't possible to measure correctly the interfacial tension for the aqueous solutions due to the fact that they were not clear, which led to a really blurred drop of crude in the tensiometer. When this occurs the error of the measurement is too high for the measure to be validated.



Figure 5 – Interfacial tension curves for the compatbility solutions.

In terms of the IFT of the compatibility solutions it can be observed that there was no correlation with the sulfate concentration.

In the solubility study no conclusions were reached.

Globally the sulfate study was considered inconclusive.

# 3.2. Influence of the change in FO concentration study

In this study the objective was to identify the influence of the free oil concentration in the evaluated parameters. In the next table it is possible to observe the compositions of the samples used in this study.

Table 3 – Composition of the mixtures used in the FO study

Sample:	Α	AB1	AB2	AB2-2	AB3	В				
Acid										
MA (%)	81,8	81,12	80,43	79,41	78,38	77,70				
FO (%)	13,7	14,68	15,67	17,14	18,62	19,60				
H₂SO₄ (%)	3,7	3,63	3,42	3,13	2,76	2,5				
H₂O (%)	0,6	0,57	0,48	0,32	0,24	0,2				
		Neu	tralized							
MA (%)	31,70	31,44	31,17	30,77	30,38	30,11				
FO (%)	9,32	10,99	12,65	15,15	17,65	19,32				
Na₂SO₄ (%)	1,98	1,95	1,91	1,85	1,80	1,76				
H₂O (%)	57,00	55,63	54,27	52,22	50,18	48,81				

In figure 6 is possible to observe that the interfacial tension increases with the increase in FO concentration.



Figure 6 – Variation of interfacial tension with salinity, for the aqueous solutions.

In figure 7, that represents the interfacial tension of the compatibility solutions, the same effect of FO concentration is visible. However the samples with higher concentration of FO (AB3 e B) show the displacement of the optimum salinity. This is an unwanted effect because it means that to use these samples it has to be at a higher salinity which can lead to problems of compatibility with the polymer.



Figure 7 – Variation of interfacial tension with salinity, for the compatibility solutions.

There were no significant changes in viscosity when the concentration of FO was altered.

Table 5, in Annex, represents the evolution of the compatibility solutions of this study. It is possible to see that the samples with higher concentrations of free oil have better compatibility with the polymer.

### 3.3. Study of the industrial sample

After the conclusion of the previous studies, an industrial sample arrived to the laboratory that had really bad compatibility with the polymer. So it was decided to use it to confirm the results of the FO study by creating 3 other samples with the addition of different amounts of free oil. The composition of the resulting samples is presented in table 4.

Table 4 – Composition of the mixtures created from the industrial sample, D.

Sample:	D	D1	D2	D3
		Acid		
MA (%)	80,5	70,05	66,57	63,93
FO (%)	15,59	26,62	30,26	33,03
H₂SO₄ (%)	3,83	3,33	3,17	3,04
H₂O (%)	0,1	0	0	0
		Neutralized		
MA (%)	58,19	52,51	50,87	49,34
FO (%)	10,72	18,97	21,99	24,24
Na₂SO₄ (%)	3,83	3,45	3,35	3,25
H₂O (%)	27,26	25,06	23,79	23,18

In figure 8, it is possible to see that the interfacial tension of the aqueous solutions suffers the expected increase, as seen in the FO study.



Figure 8 – Interfacial tension curve for the aqueous solutions.

However, when analyzing the IFT of the compatibility solutions it was noted that here the effect was not the same. The interfacial tension of the compatibility solutions decreases with the increase in FO concentration until the sample with more free oil, where it increases abruptly. This diminution is favorable to the utilization of this sample in EOR. It is suspected that there is a limit in FO concentration that allows this reduction in IFT, although, a more detailed study should be done to confirm these results.



Figure 9 – Interfacial tension curve for the compatibility solutions.

In figure 10 can be noticed that, in general, the concentration of FO does not affect the viscosity of the solutions. However, for the sample D2, it is observed a significant drop in viscosity. This sample should endure further studies of viscosity.



Figure 10 – Viscosity vs free oil concentration.

Table 6, in Annex, represents the evolution of the compatibility solutions. It can be easily noted that the sample D2 has the best performance in this parameter.

### 4. Conclusions

This work's main objective was to evaluate the influence of changing the composition of the surfactant mixture in the compatibility between polymer and surfactant. The composition of Free Oil and sodium sulfate are the components whose influence in the compatibility and efficiency was studied.

In the sulfate study wasn't reached a conclusion in the majority of the analyzed parameters.

In terms of the compatibility between surfactant and polymer there was no noticeable improvement. The transmittance values are similar and the solutions started showing precipitate without any correlation with the sulfate concentration.

When analyzing the efficiency of the solutions, i.e. the decrease induced in the interfacial tension of the system, there is no alteration related with the sulfate concentration in the sample. However, there is a chance that an increase in sulfate concentration can lead to the displacement of the optimum salinity of the formulation. More testing would be needed to confirm this observation.

In the solubility study, there were no conclusions given the fact that the solutions precipitated almost at the same time. It was expected an improvement in the solubility with the increase of sulfate in the sample, as it had been previously seen in other studies in Cepsa.

The increase in sodium sulfate led to an improvement of the viscosity. This effect is unexpected given the increase in sodium and its negative effect in the viscosity of the chosen polymer (HPAM).

When analyzing the effect of changing the Free Oil (FO) concentration in the mixture a conclusion was reached: it has two opposite effects. On one hand, the increase in FO concentration leads to an improvement in the compatibility with the polymer. On the other hand, it originates an increase in IFT, and also a displacement in the optimum salinity to higher concentrations. However, there is no influence in the viscosity of the solutions.

Although, when these conclusions were tested in the study with the industrial sample, some were not verified. The study with the industrial sample, D, had as main goal the compatibility improvement.

Initially the sample D had low compatibility with the polymer, good interfacial tension in aqueous solution that reached the interval of ultra-low tension, but the compatibility solutions didn't perform as well.

The mixtures created from the sample D, showed an improvement in compatibility and

also a significant increase in the solutions transmittance. The sample D2 was the best in terms of compatibility with the polymer, given the fact that it didn't precipitate. The improvement in compatibility can be due to the fact that FO, which is composed only by hydrocarbons, reduces the repulsive forces between the polymer and the surfactant

In terms of the interfacial tension in aqueous solutions, an increase in the free oil concentration originated the increment in IFT as seen in the influence of FO study. However, the tension of the compatibility solutions didn't behave the same way. The sample D2, which has 30% of FO, had the lowest IFT reaching values as low as  $10^{-5}$  mN/m. The sample D1 also presented a lower IFT than the original sample D. The D3 sample, however, has higher interfacial tension values, which suggests that there is a limit concentration of FO that induces the decrease of IFT. This limit must be located between 30% and 33% of FO.

Analyzing the effects of the increment in the FO concentration in the viscosity, it was noticed that, in general, there is no effect that could influence the efficiency of an EOR process. There was a decrease in the viscosity of D2's solutions that should endure a more detailed study, because it shows the possibility of an alteration in the pseudoplastic behavior.

The solubility evaluation of the samples led to the conclusion that D3 is the most soluble sample of the study, given the fact that it was the only that didn't precipitate. Between the other samples it is really difficult to make a distinction based only in observation because the precipitation occurred almost simultaneously.

Reviewing all the parameters in analysis, it can be verified that the D2 sample (which has 30% of FO in its acid form) is the one that has the best performance in the majority of the criteria. It is possible to say that this concentration of FO is the optimum value, between the analyzed values of FO. Although there are some reserves when noting this fact given the effect observed in the viscosity.

In conclusion, the concentration of sulfate in the mixtures of surfactant doesn't have an effect in the performance of the sample. On the other hand, the free oil concentration was proven to be an important variable, as it influences the majority of the parameters that are important to

the efficiency of the chemical methods of enhanced oil recovery.

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### 6. Nomenclature

CAC – Critical adsorption concentration

CEC – Critical electrolyte concentration

CMC – Critical micelar concentration

CMC2 – Critical micelar concentration in polymer presence

DF – Auxiliar surfactant

EOR - Enhanced Oil Recovery

FO – Free Oil

HPAM – Partially hidrolized polyacrilamide

IA – Acidity index

IFT – Interfacial tension (mN/m)

k – Permeability (m<sup>2</sup>)

Ko – Crude oil relative permeability

K<sub>w</sub> – water relative permeability

- LAB Linear alkylbenzene
- LAS Sulphonated linear alkylbenzene

m – Mass

- MA Active matter (%)
- MM Molar weight
- M<sub>r</sub> Mobility ratio
- N<sub>ca</sub> Capilar number
- OIP oil in place
- r Drop radius
- So Crude oil saturation
- Sor Crude oil residual saturation
- S<sub>w</sub> Water saturation
- Swr Water residual saturation
- TS Surfactant in study
- v Fluid's superficial velocity (m/s)
- V Volume

 $\Theta$  – Contact angle between a surface and a liquid drop

- $\mu$  Dynamic viscosity
- $\lambda$  Mobility
- $\Delta \rho$  Density difference
- $\Delta P$  Pressure gradient (Pa)
- $\Delta x$  Average width of the porous medium (m)
- ω Angular velocity

### 7. Annex

### Table 5 – Evolution of the compatibility solutions in the FO study.

Day 1			Day 3			Day 5				Day 7		Day 9		Day 13			Day 23			Day 35		5		
10 0	0,3	0,5	0,7	0,3	0,5	0,7	0,3	0,5	0,7	0,3	0,5	0,7	0,3	0,5	0,7	0,3	0,5	0,7	0,3	0,5	0,7	0,3	0,5	0,7
A																								
AB1																								
AB2																								
AB2-2																								
AB3																								
В																								

Table 6 – Evolution of the compatibility solutions used in the study of the industrial sample.

40°C		Da	y 1 Day 2					Day 5 Day 12							Day 15				Day 21					
40 C	0,3	0,5	0,7	0,9	0,3	0,5	0,7	0,9	0,3	0,5	0,7	0,9	0,3	0,5	0,7	0,9	0,3	0,5	0,7	0,9	0,3	0,5	0,7	0,9
D																								
D1																								
D2																								
D3																								

Table 7 – Characteristics of the crude oil used in the interfacial tension measurements.

Crude Oil										
Provenience	Colombia									
TAN (mg <sub>кон</sub> /g)	0,05									
API Grade	20 <sup>°</sup>									
Saturaded	34,10%									
Aromatics	26,90%									
Resins	21,40%									
Asphaltenes	17,60%									

Table 8 – Equipment used in the quantitative evaluation of the mixtures.

Equipment	Brand and model	Absolut error
colorimeter	Hach-Lange LICO 500 Color Measurement	0,3
viscosimeter	Brookfield DV-II+	0,06
tensiometer	Kruss Site 100	0,0004