Experimental evaluation of linear alkylbenzene sulphonates for Enhanced Oil Recovery

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Abstract

The extraction of oil from a reservoir is a difficult process to perform, not only because of its physico-chemical properties, but also by the natural conditions of the extraction place. Thus, arose the need of developing technologies that could improve the mining operations profitability and reduce operating costs.

Among the various EOR chemical processes, in this work we studied the application of surfactants (alkylbenzene sulphonate) in reducing interfacial tension between oil and water.

Initially, we assessed the behavior of surfactants in binary systems (water-surfactant) by CMC determination, yielding lower values for the 2-phenyl-alkane isomers when compared with other alkylbenzenes. We also observed that the molecular weight is a key aspect in these assays, confirming that the heaviest surfactants present the lowest values of CMC.

Subsequently, we characterized the surfactants in ternary systems of surfactant-oil-crude (SOW) using the hydrophilic lipophilic deviation (HLD) method, to determine the characteristic parameters of each surfactant. For this, we demonstrated that the molecular weight, salinity, different isomers and the addition of diverse alcohols and hydrocarbons constitute different factors that influence the surfactant behavior.

Thus, for the heaviest surfactants we demonstrated that, in addition to their higher sigma, their optimal salinities are decreased and also that they interact preferably with hydrocarbon of longer chain. For the light surfactants the opposite happens.

Relatively to the 2-phenyl-alkanes isomers, these molecules present a different behavior in the presence of this system, with a lower sigma value compared with the other isomers as well as a greater tolerance to salinity of the medium.

Keywords: Interfacial Tension, Surfactant, *EOR*, CMC, HLD, SOW.

1. Introduction

In practice, from de amount of oil that exists in the reservoir, only fraction of it is able to be extracted and used, remaining a big part of it inside (30-50 % approximately).

In order to provide sources to increase the profitability of the oil extraction, three fundamental pathways were created.

The first one is called primary recovery and uses the difference of pressures between the inside of the reservoir and the atmosphere. This process allows the extraction of 10 to 15% of the total amount of oil.

When the inside pressure of the reservoir becomes equal to the pressure from the outside it is necessary to make use of the secondary recovery. For this method is necessary to inject inside of the oil well one predetermined fluid (most commonly water), in order to increase the pressure gradient and, by this, to make possible the oil spread into the main wells and extractors, leading to one recovery of 30% of the remaining oil.

At last, when the residual concentration of the oil is reached, it becomes the third phase, called tertiary recovery or *Enhanced Oil*

Recovery, EOR, in which is applied thermal, chemical and mixed methods. At this stage it is possible to collect between 60 to 80% of oil in the reservoir. [1]

Within these chemical methods, the use of surfactant as agent is promising, since they are able to reduce interfacial tensions of crude. This allows the amplification of the displacement and, consequently, increases the recovery factor, which prompted to a growing interest of the oil industry.

1.2. Surfactants

Surfactants are amphipathic compounds, which means that are molecules that present in their constitution one hydrophilic region (soluble in aqueous medium) and one hydrophobic region (soluble in organic solvents). The presence of these two distinct regions allows adsorption at the interfaces water-air, water-oil and water-solid, Figure 1.
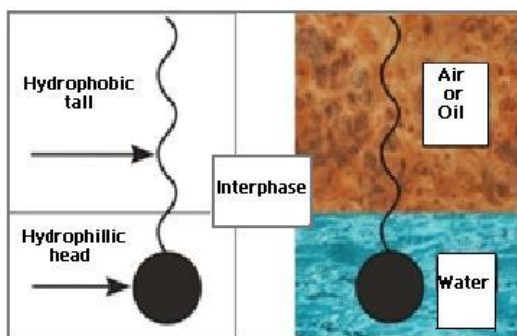

Figure 1 - Representation of a typical surfactant and your interaction in oil-water.

The polar group, or hydrophilic, nominate the surfactant. This part can be made up of several components within the ionic group (anionic or cationic), nonionic and amphoteric (which have anionic and cationic groups).

When the surfactant are dissolved, they may become monomers or aggregates, called micelle. This feature is extremely important for their use in EOR projects, and will be discussed further.

This study will focus mainly on sulfonated anionic surfactants and, particularly, on LAS (linear alkylbenzene sulfonate), Figure 2.
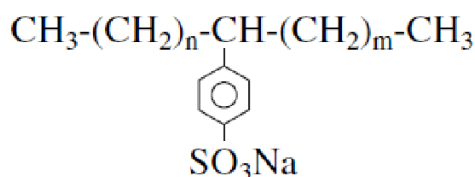

Figure 2 - General structure of LAS.

The LAS molecule contains an aromatic ring sulfonated at the para position and attached to a linear alkyl chain at any position except the terminal carbons. The alkyl carbon chain typically has 10 to 14 carbon atoms and the properties of them differ in physical and chemical properties according to the alkyl chain length, resulting in formulations for various applications. [2]

1.3. Critical Micelle Concentration (CMC)

In dilute solutions, the surfactants act as electrolytes in the form of monomers, guided preferentially to the interface, reducing the interfacial tension.

The water draw, by electrostatic forces, the polar groups while the hydrophobic portion is repelled by the aqueous phase.

Due to the different structure of the surfactant, they present a number of unique properties, being one referred as CMC.

Therefore, as you increase the amount of surfactant to be dissolved in a given solvent, tends to a limit value that determines the saturation concentration at the interface.

From this point (CMC), the interface is fully occupied by the molecules and begins the process of spontaneous formation of molecular aggregates called micelles. The various phases are observed in the following figure.
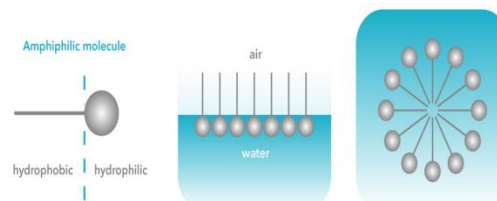

Figure 3 - Micellization.

It is important to refer that surface tension as well interfacial tension of a system containing a pure surfactant does not vary when the concentration exceeds its CMC, in other words, it can be said that an excess of micelles does not change the surface activity or interfacial.

1.4. Interfacial Tension (IFT)

The interfacial tension results from the interaction of molecules from two different phases that are in contact (gas / liquid, liquid / liquid, liquid / solid or gas / solid). The contact and interaction of these two phases causes a gradient of forces at the interface, which leads

to an accumulation of free energy in the system. Generally the IFT is expressed as a force per length and units most commonly used are dynes/cm or mN/m.

The successful application of chemical methods (which use surfactants) in ROS requires that the amount of surfactant adsorbed is reduced and the interfacial tension value ultralow, in the whole reservoir.

For the displacement of oil in the rocky reservoir pores and capillaries are needed interfacial tension values of aqueous-oil solution around of 10^{-3} mN /m, Figure 4. [3]

Figure 4 - Drop of a hydrocarbon with ultralow interfacial tensions.

The ultra-low interfacial tension is related to a phase balance between the surfactant / oil / water system. The best conditions to obtain low tensions occur when, for certain surfactant concentrations, the system is divided into three distinct phases in equilibrium with each other.

1.5. Hydrophilic-Lipophilic Deviation (HLD)

In this formulation, the interfacial tension between oil and the microemulsion is reduced so that the capillary forces that store oil within the pores of reservoir disappear or become negligible. A rating of "optimal" is used in this case as this is the formulation that allows for a maximal recovery of oil, employing a set of variables to obtain equal interactions between surfactant, water and oil, resulting in a value of HLD equal to 0.

The HLD method presents the same concept of R Winsor relation. However, the advantage is that use a single general variable for the formulation and in a more quantitative way, being possible to make the following approximation: R = 1 - HLD = 0, R> 1 - HLD> 0, R <1 - HLD <0. [4]

The HLD value is a dimensionless number and in the simplest case, the aqueous phase is a solution of sodium chloride and the oil is an n-alkane. The formula is expressed as follows:

$$HLD = \sigma + \ln sal - kEACN + t\Delta T + aA$$
(1)

Where,

σ - pârametro característico do tensioactivo considerado;

sal - salinidade da água em percentagem máxima de NaCl numa fase aquosa;

k - constante dependente do grupo hidrofílico;

$EACN$ - nº de átomos de carbono da molécula n-alcano;

t - constante;

ΔT - diferença de temperaturas, em que a tempetura de referência são 25 ˚C.

a - constantes característica do álcool considerado.

A - percentagem ponderada do álcool considerado.

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2. Material and Experimental Methods

2.1. Chemicals

Products	Manufacturer	Purity (%)	M.M (g/mol)
NaCl	Scharlau	-	58,44
n-Heptane	Scharlau	99	0,21
n-Decane	Merck	99	2,28
n-Dodecane	Acros Organics	99	0,34
Tetradecane	Cepsa Química	-	8,39
1-Butanol	Acros Organics	-	4,12
2-Butanol	Merk	99	4,12
2-Propanol	Acros Organics	-	0,1
1-Pentanol	Scharlau	-	8,15

Table 1 - Characteristics of the chemicals used and their manufacturers.

Products	LAS Na C15	LAS Na 2-fenil-C15	LAS Na C16	LAS Na 2-fenil-C16	LAS Na C18	LAS Na C20
Sulfonic acid (M.A.%)	93,7	97,2	96,9	96,3	96,3	96,0
H$_2$SO$_4$ (%)	2	1,7	1,4	0,9	1,5	1,4
Water (%)	0,6	0,6	0,6	2,3	0,6	0,6
Free Oil (%)	3,7	0,6	1,1	2,3	1,6	2
Sulfonic acid g/mol)	366	366	389	389	410	425

Sodium Sulfonate (MA %)	45,9	47,5	49,5	50,3	21,1	30
Sodium Sulfonate (g/L)	388	388	411	411	432	447

Table 2 - Fundamental characteristics of the surfactants studied.

Crudes	Origin	Density (API)	Saturated (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
Crude A	Nigeria	33.7º	47,5	25,8	25,6	1
Crude B	Iran	29.5º	25,3	47,5	18,1	9,1
Crude C	México	33º	33,1	36,4	24,7	5,9
Crude D	Azerbaijan	35.0º	60,9	21,8	16,4	0,9
Crude E	Iraq	30.5º	22,4	48,3	24	5,3
Crude F	Argelia	45º	65,6	12,9	21,3	0,2
Crude G	Colombia	20º	34,1	26,9	21,4	17,6

**Table 4 -** Characteristics and origin of crudes study.

2.2. Critical Micelar Concentration

2.2.1. Du Nouy Ring method

The critical micelar concentration was measured using the Du Nuoy method, by using the TE3 LAUDA tensiometer, in which as the time passes the Tensiometer / water solution prepared is diluted.

This method consists of placing a ring on a liquid interface and measure the force required for its posting from the surface, Figure 5. [5]

It is a fast and highly accurate method.
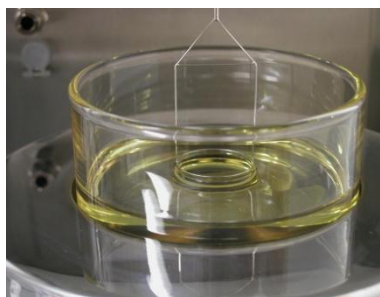
Figure 5 - Method of Du Nuoy ring.

2.2.2. Precipitation Boundary Diagram

It is used in determination of stability to water hardness ions.

Surfactant solutions with increasing concentrations are tested for each water hardness lever.

In this method, a number ranging from 0 to 5 is assigned to surfactant with varying sodium concentration depending on the apparent turbidity and precipitate formation (Table 3).

What is solution like	Value
Crystalline	0
Precipitate Excess	1
Precipitate	2
Turbid	3
Opalescent	4
Clear	5

Table 3 - Values according what is solution like.

2.3. Measurement of Interfacial Tension

In this case, the interfacial tension was measured with a Spinnig Drop Tensiometer.

The principle of measurement is based on the ratio of Vonnegut (equation 1) for an elongated droplet whose center must present a cylindrical shape. The measurement is performed in a horizontal pipe, subject to a certain speed, in which is first an aqueous solution containing a surfactant (denser phase) is introduced, and subsequently, a drop of a less dense fluid in this case oil, is submitted. [6]

$$\gamma = \frac{\Delta\rho \; \omega^2 R^3}{4} \qquad (2)$$

Where,

γ (N/m)- interfacial tension of the system;

$\Delta\rho$ (kg/m^3) - difference in densities of the aqueous and organic phase;

ω (rad/s) - angular velocity.

The centrifugal force caused by rotational movement, will produce an axial elongation of the drop of crude oil, causing it to extend increasingly as the rotational speed growths. Through the computer equipment that is connected to the tensiometer chamber, it is possible to record the drop diameter and, eventually, obtain the corresponding IFT's.

3. Results and Discussion

3.1. Critical Micelar Concentration

The purpose of this study was to determine the influence of the molecular weight, distribution of isomers and medium salinity on the amount of CMC obtained.

The results obtained by measuring the surface tension of the LASNa C16 and LASNa 2-phenyl-C16 surfactants are presented next.
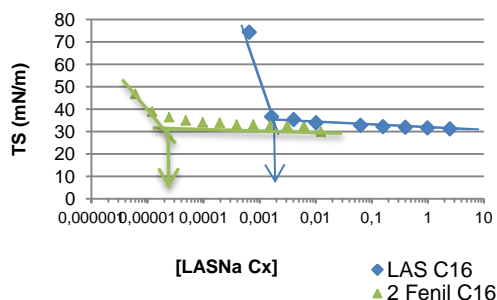

Figure 6 - Determination of CMC for C16 LASNa (0,25%) and the LASNa 2-phenyl-C16 (0,0125%) with 0.1 M NaCl.

Figure 6 compares the amount of CMC at a salinity of 0.1 M for two surfactants with the same molecular weight but different distribution of isomers. Interestingly, the LASNa 2-phenyl-C16 surfactants have a much lower CMC value (two orders of magnitude) than LASNa C16 surfactants. This is due to the external isomers (2-phenyl LASNa) that are more hydrophobic due to its more linear structure, which leads to a greater tendency to micellization, since their monomers are more stable in aqueous solution.

The next table represent the variation of salinity in order a different molecular heavy of surfactants.

	CMC (mM)	
Surfactants	0,1 M NaCl	Distilled water (without NaCl)
LASNa C16	0,0018	0,1504
LASNa C15	0,0040	0,3052

Figure 7 - CMC of surfactants LASNa C16, LASNa 2-fenil-C16, LASNa C15, LASNa 2-fenil-C15, in 0.1 M NaCl and dissolved in distilled water.

From the data obtained, it is observed that the value of the CMC decreases when the number of carbon atoms in the hydrophobic chain of the surfactant increases. This was already expected since for higher molecular weight surfactants, hydrophobic character is higher and therefore occurs a greater tendency to form micelles at lower surfactant concentrations.

3.2. Precipitation Boundary Diagram

In order to complete the region of solubility of the monomers depending on the salt concentration, several CMC assays were performed with LASNa C15 and C16 surfactants at different salinities. In Figure 8 compares the solubidade / NA tolerance diagram of the surfactants in question.
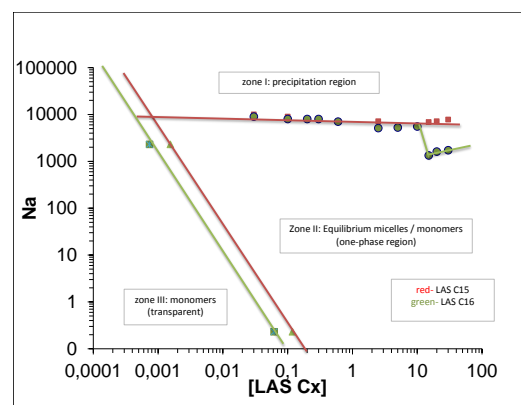

Figure 8 - Percipitation boundary diagram for surfactants LASNa C15 (red) e LASNa C16 (green).

Analyzing the graph displayed, zone I corresponds to the precipitation by salt excess (Na).

In zone II there is a balance of monomers and micelles, in which solutions are transparent, meaning that the entire salt (Na) present in the medium is tolerate.

Zone III corresponds to the solubility of the isolated monomers at lower CMC concentrations.

Note that the region of precipitation (zone I) proves to be smaller for the LASNa C15 surfactant, because it has a lower molecular weight, possessing a greater hydrophilic character, which leads to have a higher tolerance to salinity.

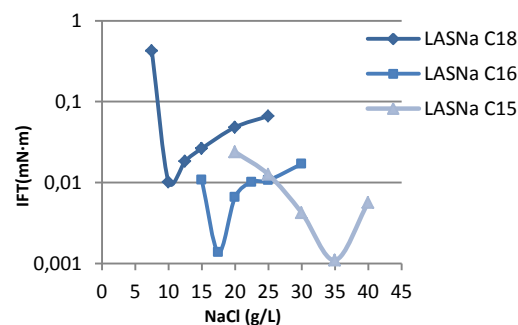### 3.3. Influence of molecular weight in measurement of IFT

Figure 9 - Interfacial tension of LASNa C18 0,5 % , LASNa C16 0,5 % e LASNa C18 0,5 % with 0,75 % 2-butanol, with heptane.

When analyzing Figure 9 is visible the influence of the molecular weight relative to the optimal salinity. That is, as the molecular weight decreases, the optimal salinity increases considerably.

This is due to surfactants having different values of sigma. The LASNa C15 presents a lower molecular weight, so the sigma value will also be lower and therefore its affinity for the organic phase decreases. Thus, by the HLD equation, it is possible to understand the higher values of optimal salinity, because the lower the sigma value is, the greater will be the value of optimal salinity so that in the end the hydrophilic lipophilic deviation, HLD, is zero.

In Table 5 presents a better view of this.

Surfactants	PM	[NaCl]$_{optimal}$
LAS Na C18	432,0	10,0
LAS Na C16	411,0	17,5
LAS Na C15	388,0	35,0

Table 5 - Optimum salinity of surfactants LASNa C18, C16, C15 and their molecular weights.

It was also studied the evolution of the sigma factor of the surfactant relating to molecular weight, with two types of alcohol, as shown in Figure 10.
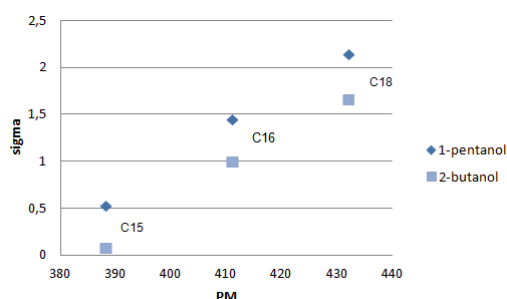

Figure 10 - Relation between PM of surfactants and sigma, σ.

Theoretically, if the same surfactants are tested with different types of alcohol, the sigma value should be the same. However, it is apparent that there is a systematic increase when 1-pentanol is used. This can be explained by the fact that 1-pentanol interacts with the surfactant at the interface, making the SOW system more hydrophobic and consequently there is an increase in the values of sigma.

Finally, in the influence of the molecular weight in sigma factor study, different isomers of different molecular weight were tested, Figure 11.
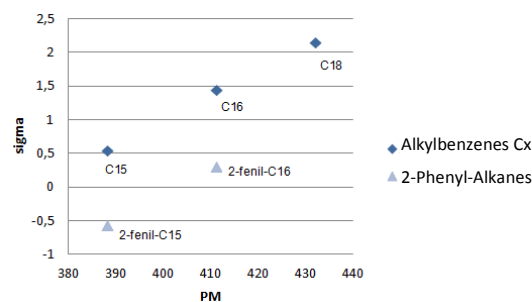

Figure 11 - Results of sigma VS molecular weight for the compounds LASNa 2-fenil-C15 and C16 and LASNa C15, C16, C18.

Results show also that the sigma, beyond depend on the PM, has different values when we have different configurations of the chain, more precisely, when tested alkylbenzenes and 2-phenyl alkanes compounds. In this figure is possible, again, to emphasize this fact and it is justified by the apparent trend of 2-phenyl alkanes compounds require higher levels to achieve the optimal salinity (HLD = 0), being more hydrophilic at the interface and present lower sigma values.

This is extremely important because in aqueous solution they have a higher lipophilicity (lower CMC). Thus, it is expected that in aqueous solution, they have a more lipophilic behavior, since at the interface, are more hydrophilic.

Finally, it is clear that the heavier surfactants have greater interaction with longer hydrocarbon chains. This assumption is then possible to observe in the diagram illustrative - Figure 12.
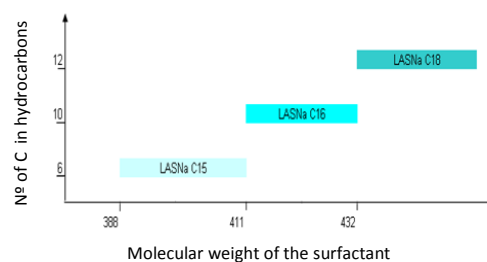

Figure 12 - Relation between the molecular weight of a surfactant and the number of carbons in hydrocarbons.

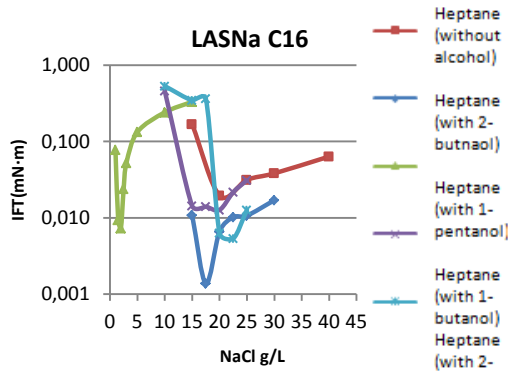## 3.4. Effect of short chain alcohols in measuring the IFT

Figure 13 - Interfacial tension of LASNa C16 0,5 %, with and without addiction of alcohol ; with heptane.

According to Table 9 (Annex), we can predict the order of increasing salinity that would be expected:

1-pentanol (1.1) <1 - butanol (0.5) <2-butanol (0.05) <2-propanol (0)

The addition of an alcohol is intended to act as a co-surfactant. Its influence can be explained by the increasing affinity for the organic phase, when it has a larger chain, and therefore their tolerance to salinity decreases. We can better understand this relationship with the equation 14, when an alcohol chain is increased, is obtained a larger amount of additive (a) and a value of salinity lower, so a desirable HLD can be reach (HLD=0).

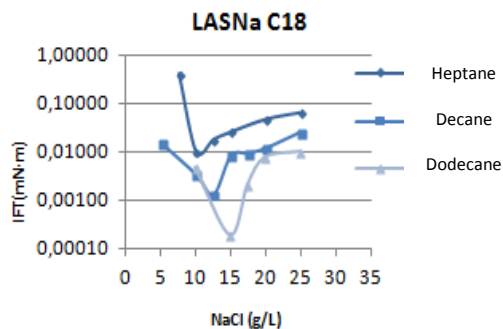## 3.5. Interfacial activity against different hydrocarbons

Figure 14- Interfacial tension of LASNa C18 0,5 %, with 0,75% 2-butanol, with different hydrocarbons.

The other surfactants that were studied are presented in the following tables.

Hydrocarbons	%NaCl	IFT (mN.m)
Heptane	35	0,001100
Decane	-	-
Dodecane	-	-

Table 6 - Results of optimal salinities and their IFT's of LASNa C15.

Hydrocarbons	%NaCl	IFT (mN.m)
Heptane	17,5	0,00138
Decane	22,5	0,000232
Dodecane	30	0,00028

Table 7 - Results of optimal salinities and their IFT's of LASNa C16.

Hydrocarbons	%NaCl	IFT (mN.m)
Heptane	-	-
Decane	2,5	0,000177
Dodecane	3	0,000508

Table 8 - Results of optimal salinities and their IFT's of LASNa C20.

As the number of carbons of the hydrocarbon is increased, from heptane to dodecane, the optimal salinity increases. This can be explained because the surfactants exhibit affinity for the organic phase, since the heavier hydrocarbon is, the more hydrophobic is the environment and therefore more salt is needed to force the passage of the surfactant to the interface and aqueous phase.

It is still visible from the data presented that there is an increasing affinity of surfactants of higher molecular weight for longer chains hydrocarbons. This means that, a heavier surfactant will preferentially interact with hydrocarbons of larger chain. For milder surfactants the opposite will succeed.

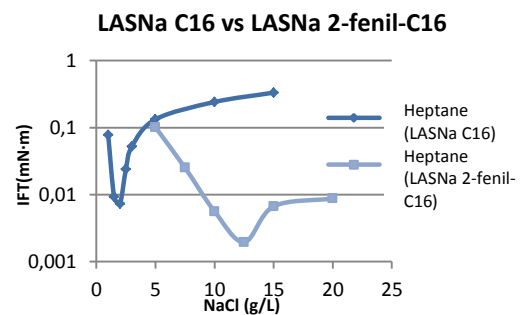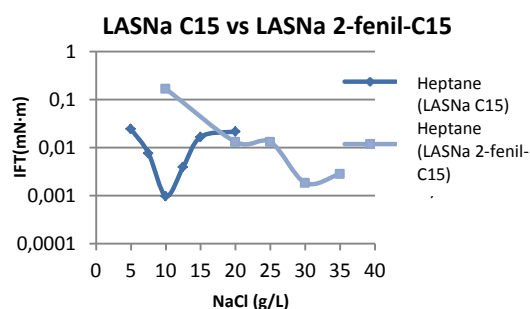### 3.6. Influence of distribution of isomers

Figure 15 - Interfacial tension of LASNa C16 and LASNa 2-fenil-C16 0,5 %, with 0,75% 1-pentanol, with heptane.
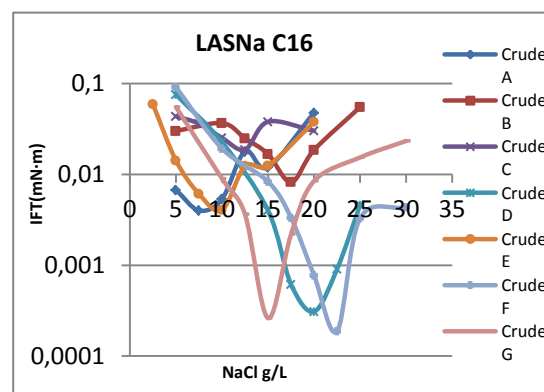
Figure 16 - Interfacial tension of LASNa C15 e LASNa 2-fenil-C15 0,5 %, with 0,75% 1-pentanol, with heptane.

The 2-phenyl alkanes surfactants are more hydrophilic than are normal surfactants and therefore, as mentioned above, its optimal salinity is higher. However at very high salinities, there is a limit of solubility of the surfactant and the solutions display as fuzzy. Thus, when 1-pentanol is added, which is a lipophilic alcohol (high coefficient in the HLD equation) yields a minimum IFT at a smaller optimal salinity and it is possible to perform a good measurement. For these reasons, the assays with 2-phenyl alkanes surfactants showed results consistent and more capable with the 1-pentanol than to 2-butanol.

In figures 15 and 16 it can be observed that the type 2-phenyl alkane influences the optimal salinity. This can be explained by the chain structure of these type of surfactants once, as is more compact, its anion (-SO3) have a greater affinity to attract positive sodium ions of NaCl, in order to improve the stability of the micelle. Allied to this, by its linear structure, the number of monomers in the interface is also increased. Therefore, due to these two reasons, the levels of salinity for this type of compounds are higher and there is a maximum interaction with the hydrocarbon, obtaining much lower values of IFT's.

3.7. Determination of interfacial tension of real crude

Figure 17 - Interfacial tension of LASNa C16 0,5% with 0,75% 2-butanol with different crudes.

For the majority of the studied crudes, the LASNa C16 surfactant is quite efficient, presenting values of IFT considerably low, on the order of 10^{-3} mN/m for the first 3 surfactants of the table 9, being the most appropriate for this surfactant.

Crudes	NaCl (g/L)	IFT (mN/m)
Crude F	22,5	0,0002
Crude G	15	0,0003
Crude D	20	0,0003
Crude A	7,5	0,0040
Crude E	10	0,0041
Crude B	17,5	0,0082
Crude C	12,5	0,0188

Table 9 - Summary table of different salinities and IFT's obtained for the tested crudes.

Thus, the LASNa C16 surfactant, high molecular weight, is suitable for the extraction of most of these crudes, excepting for crude C, since high values of interfacial tension were obtained, which leads us to believe that this surfactant is too heavy for this type of crude oil, and therefore should be tested with a lighter surfactant, such as C15 LASNa.

4. Conclusions

In the CMC study, it was concluded that an increase of the number of carbons of the alkyl chain causes a decrease in the CMC value and the presence of electrolytes in solution allows obtaining lower CMC results.

For SOW system it was concluded that there is a growing affinity of mild surfactants for a range of high salinity, while for heavy surfactants the opposite is happening.

It was also concluded that the surfactants influence the optimal formulation through the

sigma parameter (σ) characteristic of each surfactant, which increases linearly with molecular weight.

We also conclude that there is an increasing affinity of heavy surfactants for longer chains hydrocarbons.

With respect to the addition of co-surfactants, more particularly, alcohols, it is concluded that each surfactant interacts better with one type of alcohol, depending on their structure and helping to its interaction with the respective crude.

It was also concluded that the behavior of 2-phenyl-alkanes surfactants in aqueous solution does not coincide with their behavior in SOW interphase. That is, in a binary system (water-surfactant) these surfactants exhibit a very linear structure, which makes them more hydrophobic with low salinities. In a tertiary system (SOW) these surfactants behave more hydrophilic compared to normal, at interphase. This is justified by the higher sigma value, which means that its optimal salinity will be bigger.

This different behavior is related to the interaction of the hydrocarbon and also with its packaging in interphase.

Moreover, it was found that the C16 LASNa surfactant has a good affinity and interaction with crudes that present an ACN from 7 to 10.

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5. References

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Nomenclature

CMC - Critical Micelle Concentration

EACN - Equivalent Alkane Carbon Number

EOR - Enhanced Oil Recovery

HLD - Hydrophilic Lipophilic Deviation

IFT - Interfacial Tensio

K – Constant that depends on the hydrophilic group of the surfactant (*HLD*)

LAS - Linear Alkyl Benzene Sulfunate

sal (*wt% NaCl*) - salinidade da água em percentagem máxima de NaCl numa fase aquosa

SOW - Surfactant/Oil/Water

v_{rot} – Rotation speed [*rpm*]

ΔT – Difference between the operating temperature and the reference temperature [*K*]

Δρ – Density gradient [*g/cm³*]

γ (N/m)- tensão interfacial do sistema;

ω (rad/s) - Angular velocity.

σ - pârametro característico do tensioactivo considerado;

t - Constant;

a - constantes característica do álcool considerado. (HLD)

A - percentagem ponderada do álcool considerado. (HLD)

Attachments

Alcohol	a para los surfactantes	
	iónicos	noiónicos
1- ó 2- Propanol	0	-0,2
1 Butanol	+0,3 a 0,6	+0,35
2- Butanol	+ 0,05	-0,05
iso-pentanol	+1,0	+0,6
1- pentanol	+1,1	+0,7
1- Hexanol	+4	+1,1

Table 9 - Values of the parameter *a* characteristic of alcohols. [7]