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New Emulsion Containing Paraffinic Compounds

Eloi Alves da Silva Filho and Adriana Regattieri

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Abstract

Emulsions are thermodynamically unstable systems and are used in various types of industrial applications such as oil recovery, resin preparation, among many other applications. In the present work are discussed and shown data of the new emulsion system formed by components Chitosan/SDS/Hexane. The preparation and characterization of this emulsion were used the techniques of tensiometry, turbidity and flow time. The methodology requires that the participation of the paraffinic compounds as hexane, the biopolymer chitosan and the anionic surfactant Sodium Dodecylsulfate (SDS) with favorable intermolecular interactions between these three components. The results showed that a larger amount of chitosan about 85% (v/v) in the system causes of an increase in the value of surface tension, reaching 39.62 mN/m. However, high amounts of SDS about 70% (v/v) there is an increase in the turbidity values of the emulsions, with a maximum value of 110.8 NTU.

Keywords: emulsion, chitosan, surfactants, ternary systems, paraffinic compounds

1. Introduction

Emulsions are defined as dispersed systems of two or more immiscible or partially miscible liquids, the droplets of the dispersed phase having diameters ranging from about 0.1 to about 100 μm . Most emulsions are composed of an aqueous phase and an oil phase. When the oil is the dispersed phase and the water is the continuous phase, the emulsion is said to be oil in water (O/W); and when the dispersed medium is water and the oil phase is the continuous phase the emulsion is said to be water in oil (W/O). Multiple emulsions such as water in oil in water (W/O/W) consist of droplets of water suspended in larger droplets of oil which in turn are suspended in the aqueous phase [1, 2], as shown in **Figure 1**.

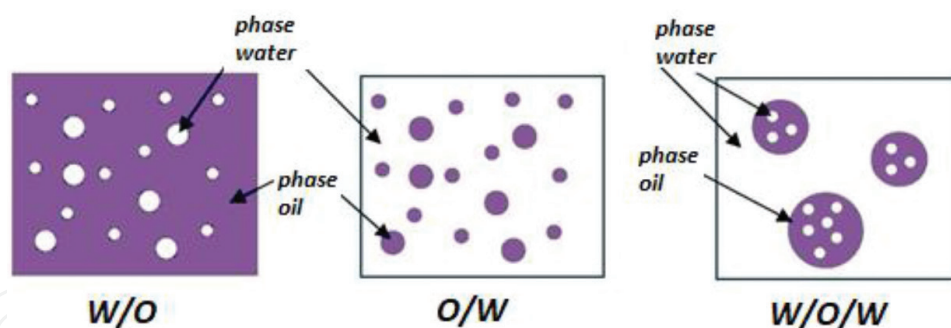


Figure 1. Different types of emulsions.

Nowadays, the number of publications on this topic has continuously grown and emulsions have attained increasing significance potential for numerous applications. O/W emulsions are generally classified into three categories depending on their stability, namely, loose, medium, and tight emulsions. Loose and medium emulsions can be easily phase separated. However, a tight emulsion causes serious problems and requires proper demulsification agents or methods to break the emulsion [3, 4]. Literature data show that emulsions of water in oil (W/O) or oil in water (O/W) are thermodynamically unstable [5]. In the present work, we report on the elaboration of a new emulsion with three components: chitosan dispersed in an aqueous phase, anionic surfactant sodium dodecyl sulfate (SDS), and hexane. One of the key aspects of the process is the stability and characterization of this emulsion.

2. Components of the emulsion

2.1. Chitosan

Chitosan is a basic linear polysaccharide or a cationic biopolymer that has many potential applications in cosmetics, tissue engineering, food and pharmaceutical industries, perhaps due to its nutritional and physicochemical properties [6, 7]. Literature has shown that chitosan can be used for heavy metal chelation, wastewater treatment, cholesterol lowering, emulsion stabilization, and it is widely available from renewable sources, obtained by deacetylation of chitin natural polymers. The molecular structure of chitosan is a β (1 \rightarrow 4)-linked linear copolymer of 2-amino-2-deoxy- β -D-glucan (GlcN) and 2-acetamido-2-deoxy- β -D-glucan (GlcNAc), shown in Figure 2, is a unique natural polyelectrolyte whose conformation and resulting properties depend on various structural and physicochemical parameters [7].

It is very important to note that chitosan consists of acetylated and deacetylated units, and the degree of deacetylation (GD) characterizes various properties of this polymer, such as acid-base and solubility properties. The basicity of chitosan increases with the degree of deacetylation due to a higher proportion of deacetylated units containing the NH_2 group. As for solubility, chitosan is insoluble in water and most organic solvents and in the emulsion process it can be a decisive factor for the stability of the emulsion [8]. The pK_a value of the free amino group is about 6.5, and thus the solubility of chitosan is also pH dependent: at pH 6.5

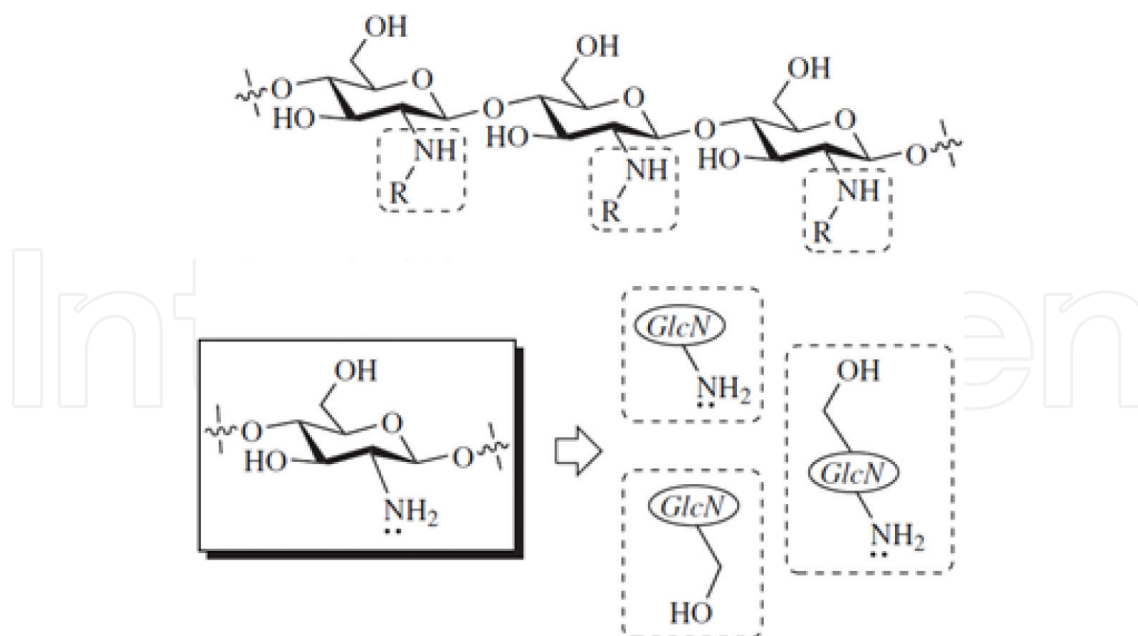


Figure 2. Molecular structure of Chitin ($\text{R}=\text{COCH}_3$) and Chitosan ($\text{R}=\text{H(GlcN)}$ or COCH_3 (GlcNAc)).

the chitosan solutions exhibit phase separation, whereas at $\text{pH} < 6.5$ is soluble and has a positive charge due to the presence of protonated amino groups [8, 9]. The different chemical modifications of chitosan and applications in biomedical, tissue engineering are summarized by Alves and Mano [10].

2.2. Surfactants and paraffinic compounds in the emulsion

The surfactants are compounds that can contribute to the stability of the emulsion. The surfactants, which are characterized by lowering the surface or interfacial tension of a system and can be classified according to the molecular structure of the polar part in: cationic, anionic, neutral and amphoteric. Effects of polymer/surfactant interactions are useful in practice to achieve emulsification, colloidal stability, viscosity enhancement, gel formation, and solubilization. For this reason, interactions between polymers and surfactants in aqueous solutions have been the subject of a lot of research, a number of reviews and papers [11]. Solid particle stabilized emulsions (Pickering emulsions) have been extensively studied because of the superior stability. Equivalent to the hydrophilic-lipophilic balance (HLB) number of the surfactants, the wettability of the particles, characterized by the contact angle, is decisive for the stability of Pickering emulsions [12]. For surfactants present in oil water mixtures, the system HLB number is the most important variable in determining whether aggregated surfactant (micelles or microemulsion droplets) resides in either water, oil or a third phase [13]. The anionic surfactant sodium dodecylsulfate (SDS) and the cationic CTAB have dynamic associations with the ions present in the system with the cationic chitosan copolymer. The neutral surfactant of Triton X-100® does not interact significantly with the aqueous system, since the hydrophobic interactions are considered of nature weak. Saturated hydrocarbons, also called alkane or paraffinic compounds, are those in which the carbon and hydrogen atoms are

bound only by simple bonds [14]. In general, hydrocarbons represent about 90% of the crude oils and depending on their gravity oils are classified by the American Petroleum Institute (API). The °API gravity of oil varies from 8.5 for very heavy crude oils to 44 for light crude oils, 20 the higher the value the better and lighter the oil [15]. Barradas et al. [16], report that oils and surfactants exhibit specific HLB values and when there is addition of a surfactant, or a mixture thereof, with HLB values corresponding to the HLB value of the oil, it is possible to reduce to the maximum the interfacial tension between the oil and aqueous phases. A mixture of surfactants with HLB values corresponding to the oil phase values may provide improved solubility and stability to a dispersed system. The choice of surfactant may also be related to its high degree of compatibility with other components of the formula, good chemical stability and low toxicity. Combining different polarities of the two agents in the surfactant system leads to important changes in the HLB values of the systems studied [16].

3. Experimental techniques

The methodology for preparing the emulsions was performed using different SDS/chitosan/hexane component mixtures as can be seen in **Table 1** and illustrated through the ternary diagram in **Figure 3**. The SDS surfactant and the chitosan copolymer were dissolved in acetic acid solution 0.2 mol/L. Each emulsion was prepared three times with volumes of 50 and 100 mL,

Emulsion	Chitosan	SDS	Hexane
1	10	85	5
2	10	80	10
3	15	70	15
4	20	60	20
5	25	60	15
6	20	70	10
7	25	70	5
8	30	60	10
9	40	50	10
10	85	10	5
11	33	33	33
12	5	80	15
13	0	95	5
14	95	5	0
15	40	60	0

Table 1. Composition of emulsions in % (v/v).

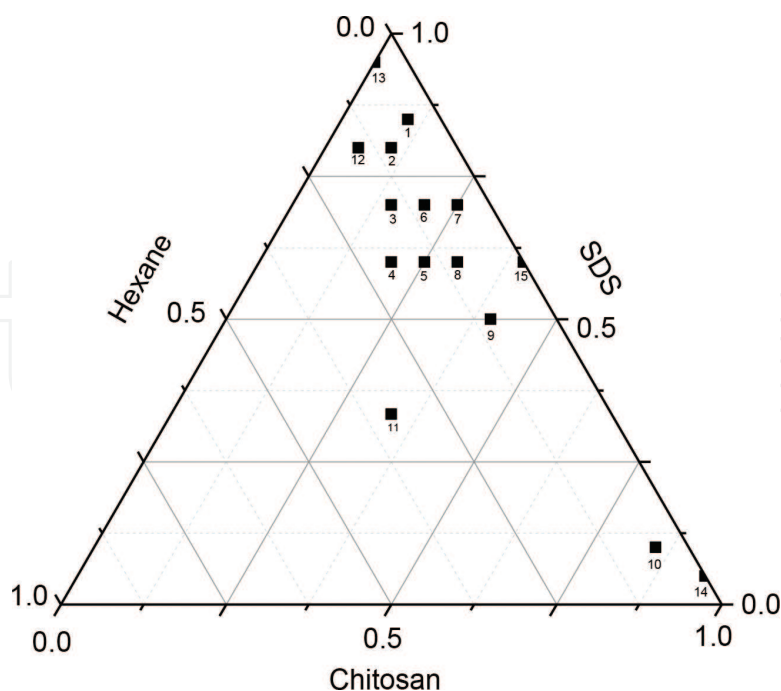


Figure 3. Ternary diagram for the emulsion compositions studied.

stirred for 7 minutes at 9000 rpm on the IKA Ultra Turrax T25 equipment. A 50 mL emulsion was stored for monitoring with respect to time. The other 50 mL and of 100 mL were used for the characterization techniques. So that the emulsions maintained a final composition of 100% (v/v), making it impossible to maintain more than one composition in % (v/v) constant of the emulsion, the other two will also be changed. Therefore, there is no possibility of changing the emulsifying system. The hexane component was used in two ways to compare the results. One was pure industrial hexane and the other hexane obtained via petroleum distillation of density equal to 88.9 °API. Samples of distilled hexane were supplied by the NCQP-UFES distillation Laboratory.

The stability of the emulsions was studied using the bottle test, observing the phase separation with time. The prepared emulsions were transferred to graduated glass vials, sealed with a plastic cap and stored at room temperature. The phase separation of the emulsion was monitored visually at regular time intervals. The emulsions were initially characterized by the calculation of the emulsification index. In 2007, studies were also carried out in which the emulsification index was calculated [17] used the volume measurement, and Techaoei et al. [18], which measured the height of the emulsion formed. The emulsions prepared produced a lot of foam, which made it difficult to calculate by volume and height measurement. The emulsions prepared produced a large amount of foam, which made it difficult to calculate by volume and by height measurement. A new emulsification index (EI) calculation method (Eq. (1)) was used to prioritize the foam formed in the emulsion, calculated by the ratio between the mass of the sample before and after of the emulsification procedure in the equipment Ultra Turrax.

$$\text{Emulsification Index} = \frac{\text{Mass of sample after of the emulsification}}{\text{Mass of sample before emulsification}} \times 100\% \quad (1)$$

Subsequently, with 48 hours of rest and phase separation, 20 mL aliquots of the dispersed (lower) phase of each emulsion were removed and surface tension measurements (Lauda Tensiometer model TD3) were performed by the method DeNöuy, and turbidity (Orbeco-Hellige Model 966 Portable Turbidimeter). In comparison, surface tension has values between 31.85 and 38.99 mN/m and for water, acetic acid and chitosan the surface tension is higher than 57.10 mN/m showed in **Table 2**.

In the different emulsion compositions (**Table 1**) shown in the ternary diagram (**Figure 3**). A larger volume of the SDS solution (>60% (v/v)) in a smaller volume of the other components of the system maintains its thermodynamic stability, that is, time for phase separation. Also discussed in a paper by Resende et al. [19] that microemulsions (transparent, homogeneous and thermodynamically stable systems) and presented similar results in the ternary diagram.

The measured values of surface tension, turbidity and flow time to characterize the emulsions are shown in **Table 3**, **Figures 4** and **5** respectively.

Figure 4 shows a comparison between the values of the data obtained by measures of surface tension, turbidity and run-time and it is observed that the values of turbidity are the ones that vary the most with the change of composition of the emulsions. Thongngam and McClements [6] studied the interactions between chitosan and SDS. They found that the progressive addition of SDS causes a greater turbidity of the solutions with chitosan, due to the formation of an insoluble complex between these two substances. This complex can be stabilized by ion-dipole and hydrophobic interactions and can be formed even when the concentration of surfactant is below the critical micelle concentration (CMC). In the systems studied in this work the SDS surfactant solutions are in a concentration above CMC, wherein such solutions are more stable. In emulsions where the SDS surfactant is at a concentration below 12 mmol/L the turbidity values are considerably low (<5 NTU). The turbidity begins to increase the extent to which there is more SDS in the emulsion and reaches its maximum value (110.8 NTU) in the emulsion whose % (v/v) composition of chitosan, SDS and hexane is 15, 70 and 15, respectively. This composition represents the saturation of chitosan with SDS and it is where the strongest interaction occurs between the components, because it was the dispersed (lower) phase of the

Solution	Surface tension (± 0.02 mN/m)
SDS 0.02 mol/L	32.13 \pm 0.64
CTAB 0.002 mol/L	38.99 \pm 0.78
Triton X-100® 0.001 mol/L	31.85 \pm 0.64
Water	72.40 \pm 1.45
Hexane	18.29 \pm 0.37
Acetic acid	69.79 \pm 1.39
Chitosan 0.37% (m/v)	57.10 \pm 1.14

Table 2. Surface tension of solutions.

Emulsion	Chitosan	SDS	Hexane	Surface tension (± 0.02 mN/m)	Turbidimetry (± 0.1 NTU)	Flow time (± 0.01 s)	[SDS] (mmol/L)
1	10	85	5	31.35 ± 0.63	53.0 ± 5.3	15.08 ± 0.15	17
2	10	80	10	30.84 ± 0.62	57.5 ± 5.8	25.83 ± 0.26	16
3	15	70	15	31.35 ± 0.63	110.8 ± 11.1	22.36 ± 0.22	14
4	20	60	20	18.86 ± 0.38	3.4 ± 0.3	25.92 ± 0.26	12
5	25	60	15	28.88 ± 0.58	1.8 ± 0.2	26.03 ± 0.26	12
6	20	70	10	31.45 ± 0.63	93.8 ± 9.4	22.07 ± 0.22	14
7	25	70	5	34.36 ± 0.69	58.7 ± 5.9	22.12 ± 0.22	14
8	30	60	10	31.73 ± 0.63	16.2 ± 1.6	26.44 ± 0.26	12
9	40	50	10	36.26 ± 0.73	2.4 ± 0.2	27.05 ± 0.27	10
10	85	10	5	39.62 ± 0.79	4.5 ± 0.5	22.74 ± 0.23	2
11	33	33	33	37.95 ± 0.76	2.7 ± 0.3	27.73 ± 0.28	6.6
12	5	80	15	31.86 ± 0.64	35.9 ± 3.6	17.10 ± 0.17	16
13	0	95	5	32.83 ± 0.66	3.4 ± 0.3	15.12 ± 0.15	19
14	95	5	0	37.38 ± 0.75	5.3 ± 0.5	25.12 ± 0.25	0
15	40	60	0	36.23 ± 0.72	0.3 ± 0.1	20.67 ± 0.22	12

Table 3. Date of emulsions analyzed.

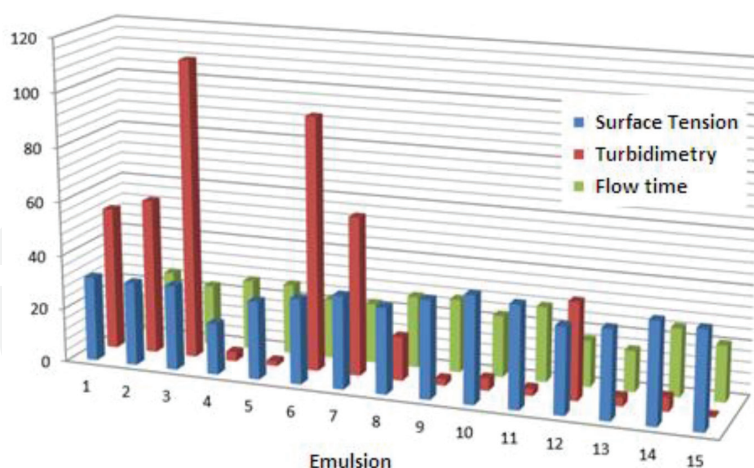


Figure 4. Comparative representation of emulsion properties.

emulsion that remained more stable (with the same appearance) over time. Turbidity is mainly due to changes in the size of the SDS-chitosan complexes and the presence of hexane. It is also verified that, when the SDS concentration is 14 mmol/L, an approximately linear increase in turbidity value occurs, with decrease of chitosan and increase of hexane. The concentration of 14 mmol/L of SDS in the emulsion is the limiting value of the system organization, because

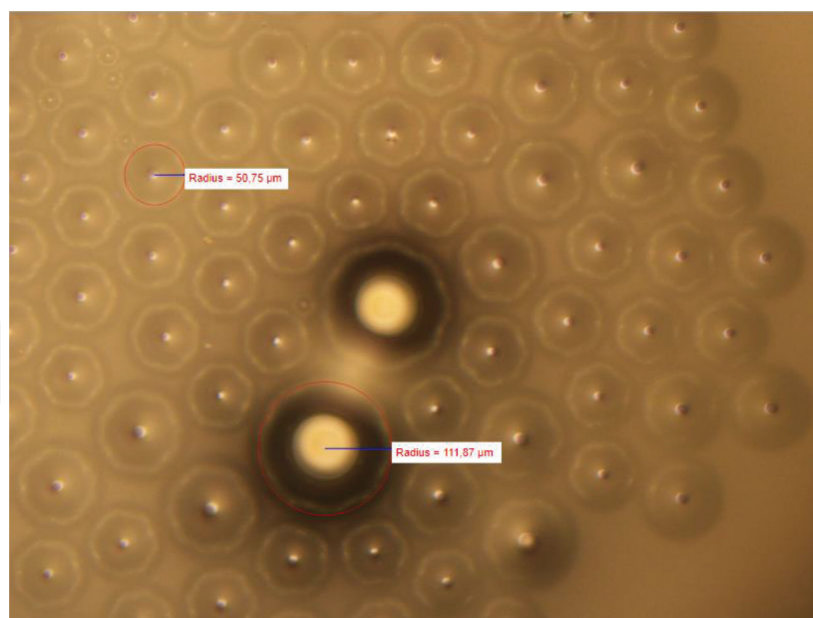


Figure 5. Separation of the phases in emulsion 3.

with the surfactant at 16 mmol/L, there is a change in the behavior of the system and then the emulsion turbidity decreases with increasing amount of hexane and decrease of chitosan.

The solution of chitosan 0.37% (m/v) presented the value of 57.10 mN/m and the hexane value of 18.29 mN/m of surface tension (**Table 2**). It can be observed in the surface tension values recorded for the emulsions that the emulsion with 85% (v/v) chitosan presented the highest value, 39.62 mN/m, and the hexane composing 20% (v/v) presented, 18.86 mN/m (**Table 3**). This demonstrates that such results are influenced by chitosan and hexane. Except for emulsions with considerable concentrations of chitosan and hexane, emulsions with SDS concentrations between 10 and 14 mmol/L presented practically constant values of surface tension which shows the predominance of a more organized in the form of micelles, since the CMC of the SDS is around 5 mmol/L. The higher flow times were observed in the emulsions where the concentrations of the three substances in the emulsion are in the closest values, due to more intermolecular interactions occurring in higher concentrations of the molecules present in the medium. As for the flow times, the emulsions with hexane P.A. showed times greater than the values recorded for emulsions with the petroleum distillate hexane.

To SDS surfactant the turbidity value with petroleum distilled hexane was lower than with P.A. hexane, a decrease of 66.3 NTU. This significant difference in the turbidity value for the SDS emulsion shows that the components present in the petroleum distilled sample may influence the formation of the SDS-chitosan complex. From the optical microscopy images the coalescence of the emulsions was observed, irreversible process in which there is separation of phases. For the systems with different surfactants the surface tension measurements show the influence of the surfactant in the emulsion, since the measured values approximate the values of pure surfactant solutions. For the SDS surfactant the turbidity value with petroleum distillate hexane a significant decrease, which shows influence of the components present in the petroleum distillate sample on the formation of the SDS-chitosan complex. Optical microscopy images were recorded in the same region of the emulsion 3 (**Table 1**) and the microscope slide was not

moved along all the images. These images are after 30 minutes the preparation of the emulsions, until the separation of the phases, and are in the order of 100 μm , showed in **Figure 5**. The phenomenon of coalescence, process of regrouping of the droplets in the dispersed phase in which the phase separation of the emulsion is observed. With this, the foam bubbles of the emulsions generally increase in size until they are close in sizes, where the phases are separated.

4. Conclusions

The systems studied in this work the SDS surfactant solutions are in a concentration above CMC, wherein such solutions were more stable. In emulsions where the SDS surfactant is at a concentration below 12 mmol/L the turbidity values are considerably low (<5 NTU). The turbidity begins to increase the extent to which there is more SDS in the emulsion and reaches its maximum value (110.8 NTU) in the emulsion whose % (v/v) composition of chitosan, SDS and hexane is 15, 70 and 15, respectively. Was also observed in the emulsion after standing is related to the amount of paraffinic compounds present in the system, since the higher the amount of hexane, the more foam. The longer flow times were observed in the emulsions where the concentrations of the three components are in the closest values in the emulsion. On the foam of each emulsion, it is observed that as the amount of hexane increases, more foam is formed. In this way, we can say that hexane is responsible for the foam of the emulsion, because of its high volatility and ability to include air bubbles to the emulsions. Regarding the hexane P.A. and petroleum distillate, it was observed that, for the surface tension values showed no significant change in the emulsions. Emulsions with hexane P.A. showed higher flow times than the values recorded with petroleum distillate hexane. This work showed that a larger amount of chitosan about 85% (v/v) in the system causes of an increase in the value of surface tension, reaching 39.62 mN/m and to high amounts of SDS about 70% (v/v) there is an increase in the turbidity values of the emulsions, with a maximum value of 110.8 NTU. Finally for the SDS surfactant the turbidity value with petroleum distillate hexane have a significant decrease and it is can contribute in emulsification of the paraffinic compounds and formation of the SDS-chitosan complex.

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Author details

Eloi Alves da Silva Filho* and Adriana Regattieri

*Address all correspondence to: eloi.silva@ufes.br

Department of Chemical, Federal University of Espírito Santo, Vitória, ES, Brazil

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