



Physical properties of botanical surfactants

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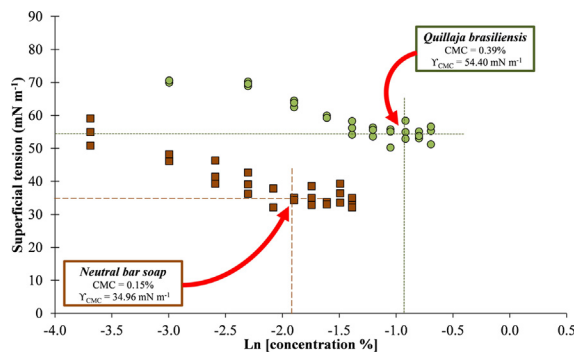
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HIGHLIGHTS

- Botanical surfactants may be suitable to the organic products sprayings.
- Some surfactants properties of *Q. brasiliensis* and *A. angustifolia* were studied.
- Different methods of preparation and concentration were evaluated.
- Dry and grind samples resulted in higher foam column height in both species.
- *Q. brasiliensis* was less able to reduce the superficial tension than neutral soap.

GRAPHICAL ABSTRACT



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ABSTRACT

Some vegetal species have saponins in their composition with great potential to be used as natural surfactants in organic crops. This work aims to evaluate some surfactants physical properties of *Quillaja brasiliensis* and *Agave angustifolia*, based on different methods of preparation and concentration. The vegetal samples were prepared by drying and grinding, frozen and after chopped or used fresh and chopped. The neutral bar soap was used as a positive control. The drying and grinding of samples were the preparation method that resulted in higher foam column height in both species but *Q. brasiliensis* was superior to *A. angustifolia* in all comparisons and foam index was 2756 and 1017 respectively. Critical micelle concentration of *Q. brasiliensis* was 0.39% with the superficial tension of 54.40 mN m^{-1} while neutral bar soap was 0.15% with 34.96 mN m^{-1} . Aspects such as genetic characteristics of the species, environmental conditions, and analytical methods make it difficult to compare the results with other studies, but *Q. brasiliensis* powder has potential to be explored as a natural surfactant in organic farming. Not only the surfactants physical properties of botanical saponins should be taken into account but also its effect on insects and diseases control when decided using them.

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1. Introduction

The management of insects and diseases in organic production systems is a great problem for farmers yet that, somehow, can limit the

expansion of cultivated areas. If on the one hand researchers have devoted great efforts in searching for effective natural products, the same can't be said for the formulation of these products. In general, botanical extracts and plant protectors are applied directly on crops without adjuvants and its efficiency depends on both the bioactivity of the active principle and also its ability to establish an interface with the target organism. The surface of the leaves of most plant species that are interesting for agriculture is formed by a cuticle composed of aliphatic and apolar substances with strong hydrophobic activity which reduce the

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level of wetness by the product (Müller and Riederer, 2005). The use of surfactants (or tensioactives) can help to overcome this barrier since it modifies positively the physicochemical properties of the botanical extract to be applied (Iost and Raetano, 2010). The surfactants generally enables an uniform product spreading on the surface of the leave, increasing the drop retention, helping the product penetration, preventing the formation of product deposits on the leaves by crystallization and reducing losses caused by rain washing (Baseeth and Sebree, 2010; Mendonça et al., 2007; Queiroz et al., 2008). An efficient surfactant must have low critical micelle concentration (CMC), which is a characteristic directly related to the amount of surfactant required to reduce the superficial tension of the product to the lowest value (Mulligan, 2005).

The saponins are secondary metabolites glycosylated which are found in a wide range of plant species that have great use in food, cosmetic and pharmaceutical industries (Cheok et al., 2014; Sparg et al., 2004), since they are considered efficient, low cost and safe for the environment and health (Basu et al., 2015; Böttcher and Drusch, 2016; Muntaha and Khan, 2015). Among the saponins physicochemical features their ability to form persistent foam in aqueous solutions and with high interfacial activity is one of the most important resources for developing surfactants (Böttcher and Drusch, 2016; Ribeiro et al., 2013), especially for botanical extracts application (Chapagain and Wiesman, 2006).

However, the content and the composition of saponins in plants, and therefore their own bioactivity, are determined both by its botanical origin (Böttger et al., 2012; Mert-Türk, 2006) and the biotic and abiotic factors involved, such as herbivory, development stage, cultivation techniques and environmental variables (Costa et al., 2013; Szakiel et al., 2011).

Some species in southern Brazil have saponins in their composition with great potential to be used as natural surfactants for spraying organic crops. *Quillaja brasiliensis* (A. St.-Hill. & Tul.) Mart. (Quillajaceae) is a native tree also known as soldier-soap or soap-dish due to its leaves and bark that produce persistent foam in water (Carvalho, 2006; Yendo et al., 2015). *Agave angustifolia* Haw. (Agavaceae), in turn, is native from Mexico, where other species of this kind have economic importance in beverage industry and folk medicine (Ahumada-Santos et al., 2013; Good-Avila et al., 2006) and that is used mainly as ornamental specie in Brazil.

This work aims to evaluate some surfactants physical properties of *Quillaja brasiliensis* and *Agave angustifolia*, based on different methods of preparation and concentration.

2. Material and methods

2.1. Site, collection and preparation of botanical material

The study was conducted at the Estação Experimental Cascata (EEC), Embrapa Clima Temperado, Pelotas, Brazil. The plants were collected from September 2014 to March 2015. The *Agave angustifolia* sample was collected at Universidade Federal de Pelotas area in full sun, Capão do Leão county (31°48' S, 052°24' W, 13 m a.s.l.), and the *Quillaja brasiliensis* sample was taken on the forest extract edge, in the EEC area (31°37' S, 052°31' W, 180 m a.s.l.). The plant samples were submitted to three preparation procedures. A fraction of each species were dried in a forced air circulation oven at 40 °C during 24 h and 168 h for *Q. brasiliensis* and *A. angustifolia* samples, respectively, and after that, they were pulverized with an electric grinder, sifted into a 2 mm mesh, packed in amber glass, stored at room temperature, and protected from light. Other fraction of samples were packed in sealed plastic bags and stored in a freezer for 7 days. For the testing, the samples were naturally defrosted and fractionated into 5 × 5 mm pieces. The third fraction, fresh samples (*in natura*) were just fractionated into 5 × 5 mm pieces.

2.2. Analyzes

2.2.1. Foam height column and foam index (FI)

For each plant species and preparation procedure it was developed a sequence of concentrations from 0.2 g to 2 g at intervals of 0.2 g, to which it was added 200 mL of distilled water. Then, the samples were submitted to a decoction period of 5 min. After cooling, each decoction was filtered through cotton and distributed in test tubes (17 × 182 mm) in successive series of 1, 2, 3, up to 9 mL, adjusting the final volume to 10 mL. The last test tube received 10 mL of the undiluted integral decoction. It was measured the pH of each decoction with an indicator strip and, when it was necessary, there was a correction to 7.0 with calcium carbonate. Test tubes were shaken by hand for 15 s and remained resting for 15 min, when it was measured the height of persistent foam column in each treatment. The determination of foam index was made adapting the methodology described in Brazilian Pharmacopoeia (Brasil, 2010a) and it was calculated by the equation:

$$FI = 10 / [(M \cdot Ddv) / 200] \quad (1)$$

where M (g) is the plant mass for each treatment and Ddv (mL) is the decoction-diluted volume used in each test tube. The 10 and 200 values represent the total volume in the test tube and the volume used in decoction, respectively. FI is an index presented without any unit of magnitude and represents the highest dilution in which a given mass of plant is able to form 1 cm column of foam under specific conditions, thus enabling their comparison with different saponins solutions.

2.2.2. Superficial tension and critical micelle concentration (CMC)

From the FI results it was determined the static superficial tension only for *Q. brasiliensis* in the decoction concentrations of 0.25% and 0.5%. As elements of comparison, it was also evaluated the decoction at 2.5% and neutral bar soap (NBS) at 0.25%. It was used the drop weight method, adapting the procedure described by Lee et al. (2008). From a burette, it was gathered 20 drops of each dilution decoction, in triplicate, and it was measured the average value of the mass and drop volume. The superficial tension was calculated by Tate Law and it was added a correction factor concerning to the remaining fraction of liquid at the burette tip (Lee et al., 2008):

$$\gamma = (m \cdot g) / [2 \cdot \pi \cdot r \cdot \Psi(r/V^{1/3})] \quad (2)$$

where γ is the superficial tension (mN m^{-1}), m is the average mass (g) of each drop, g is the gravity acceleration (980 cm s^{-2}), r is the radius of the burette tip (0.175 cm) and $\Psi(r/V^{1/3})$ is the correction factor, calculated by equation:

$$\begin{aligned} \Psi(r/V^{1/3}) = & 1.000 - 0.9121(r/V^{1/3}) - 2.109(r/V^{1/3})^2 \\ & + 13.38(r/V^{1/3})^3 - 27.29(r/V^{1/3})^4 \\ & + 27.53(r/V^{1/3})^5 - 13.58(r/V^{1/3})^6 + 2.593(r/V^{1/3})^7 \end{aligned} \quad (3)$$

where V is the average volume (cm^3) of each drop.

The critical micelle concentration (CMC) is the concentration from which the surfactant addition no longer affects the superficial tension of the solution (Böttger et al., 2012). CMC was determined by correlating the superficial tension values with the logarithm of each decoction dilutions concentration (Jian et al., 2011). It was plotted a linear regression to the previous values to the point of inflection and another one to the subsequent values. The CMC point is the intersection of these two lines.

2.3. Statistical procedure

The evaluation of foam height column was carried out as a completely randomized design with two species, three methods of preparation,

ten concentrations, ten dilutions factors and three replications ($n = 1800$). The data did not confirm the presuppositions to parametric analysis and therefore were submitted to the non-parametric Kruskal-Wallis test (χ^2) and the averages were compared by Simes-Hochberg method ($p < 0.05$). For the evaluation of superficial tension, the design was considered only to *Q. brasiliensis* again, with four concentrations in ten different dilutions and three repetitions, besides the control of NBS ($n = 150$). At last, the CMC was evaluated with *Q. brasiliensis* and NBS each one in ten dilutions and three replications ($n = 60$). Power regression curves were used to verify the tendency of the treatments concerning to foam height column, foam index, decoction concentrations and the superficial tension.

3. Results and discussion

3.1. Foam height column and foam index (FI)

3.1.1. Evaluation of species, methods of preparation and concentration

The foam height column values showed statistical differences between species, methods of preparation and concentration, as well as within each species with respect to procedures and concentrations (Table 1).

The drying and grinding of the plant material was the method of preparation that resulted in higher foam column height in both species. There was no difference between the use of fresh (*in natura*) or frozen material, and their values were lower than 50% of those observed in drying and grinding procedure (Fig. 1).

The drying of the plant material and their grinding, with some exceptions, is the most common method of preparation for the saponins extraction (Cheok et al., 2014) and it is recommended for FI determination by the Brazilian Pharmacopoeia (Brasil, 2010a). Drying of the material concentrates the saponin and possibly improving the qualitative test results (Agustini et al., 2015). However, it can't be disregarded the use of fresh plants or the freezing conservation by family farmers without drying devices. Possibly, in these cases, plant mass should be increased to compensate the water content.

Between the species, *Q. brasiliensis* produced foam height column values higher than the ones observed in *A. angustifolia* for the three methods of preparation, suggesting a higher saponin content. Moreover, the interfacial behavior of a botanical extract is associated with the aglycone structure as well as the sugar chains (Böttcher and Drusch, 2016; Pagureva et al., 2016). Saponins present in the *Q. brasiliensis* are the triterpenoid type (Costa et al., 2013) while in the *A. angustifolia* are the steroid type (Sidana et al., 2016). In this sense, the triterpenoid saponins are associated with the higher viscoelastic interfacial layers and this lead to a high foamability and foam stability when compared to steroid saponins (Böttcher and Drusch, 2017).

Nevertheless, it is important to consider the longest time required for drying of *A. angustifolia* than *Q. brasiliensis*, which may have affected the difference in amount. In other studies, it's observed that *Moringa oleifera* leaves dried in drying oven, in the shade or in the sun did not affect the saponin content (Adeyemi et al., 2014), but *Chlorophytum borivilianum* roots dried at higher temperatures and more intense forced ventilation showed lower saponins percentage when dried in the shade or in the

sun (Agrawal et al., 2013). Saponin content in Agave genus was also affected by phenological stage and by the chemistry structure of sapogenin involved in it (Leal-Díaz et al., 2015). Moreover, some authors consider that *A. angustifolia* has a low content of saponins (Ahumada-Santos et al., 2013).

Comparing only the dried and grinded samples, the results show that the foam height columns produced by *Q. brasiliensis* decoctions were superior to the ones produced by *A. angustifolia* in both concentrations and all dilutions (Fig. 2).

Biotic and abiotic factors, such as the herbivory and pathogens, light, moisture and soil fertility, also interfere in saponins production (Costa et al., 2013; Szakiel et al., 2011). Plant samples were collected from different areas and under distinct stress conditions also, which it implies to consider that exogenous factors may have possibly contributed to part of this difference.

The neutral bar soap (NBS) to 0.25%, in turn, even in the lower decoction volume (equivalent 0.025% concentration), formed a foam height column above 8 cm, higher than the best treatment: *Q. brasiliensis* to 1% in decoction volume 10 (full decoction undiluted).

3.1.2. Foam index (FI) and correlation of variables

The FI of *Q. brasiliensis* samples prepared by dry and grinding method reached value of 2756, while the *A. angustifolia* sample achieved only 1017. Just to compare, the value of reference for the *Q. saponaria* powder is at least of 1000 in the Brazilian Pharmacopoeia (Brasil, 2010b).

From these results, next evaluations were performed only with *Q. brasiliensis* prepared by drying and grinding methods. The foam height column showed high correlation with both FI and the solution concentration, allowing the construction of power regression curves, with high determination coefficient ($r^2 = 0.9249$) (Fig. 3).

In practical terms, due to the high correlation between variables, it is possible to determine the FI and the concentration of a *Q. brasiliensis* surfactant solution by a simple measurement protocol.

3.2. Superficial tension

3.2.1. Evaluation between concentrations and critical micelle concentration (CMC)

The superficial tension of the *Q. brasiliensis* decoctions and the neutral bar soap (NBS) in all dilution factors tended to decrease with the increasing of concentration and showed high determination coefficients (r^2), above 0.90, except in 0.25% *Q. brasiliensis* concentration (Fig. 4).

It's possible to observe that the NBS was much more effective in reducing superficial tension than *Q. brasiliensis*. The superficial tension of NBS was about 71% than observed for *Q. brasiliensis* 2.5% in dilution factor 1. A good surfactant is the one that has the potential to reduce the water superficial tension from 72 to 35 mN m⁻¹ (Mulligan, 2005; Santos et al., 2016). The full decoctions undiluted of *Q. brasiliensis* 2.5% and 0.5% produced a surfactant effect equivalent to 0.10% and 0.75% of mineral oil concentration or 0.025% and 0.10% of vegetable oil. SNB 0.25% surfactant effect, in its turn, is similar to 0.50% concentrations of these same oils (Mendonça et al., 2007).

Although less efficient to reduce superficial tension when compared to SNB, *Q. brasiliensis* results are similar to those verified with *Sapindus*

Table 1

Hypothesis test (χ^2) to the foam height column among different species, methods of preparation and concentrations, in full undiluted decoction.

| | General | | | Species | | | | | |
|----------------|---------|----------|------------------------|------------------------------|----------|------------------------|---------------------------|----------|------------------------|
| | DF | χ^2 | $p < 0.05$ | <i>Quillaja brasiliensis</i> | | | <i>Agave angustifolia</i> | | |
| | | | | DF | χ^2 | $p < 0.05$ | DF | χ^2 | $p < 0.05$ |
| Species | 1 | 55,66 | 8,61 e ^{-14*} | – | – | – | – | – | – |
| Methods | 2 | 67,44 | 2,26 e ^{-15*} | 2 | 43,90 | 2,92 e ^{-10*} | 2 | 57,45 | 3,34 e ^{-13*} |
| Concentrations | 9 | 41,29 | 4,43 e ^{-6*} | 9 | 38,64 | 1,34 e ^{-5*} | 9 | 19,93 | 0,0183* |

DF – degrees of freedom.

* Significant differences using the Kruskal-Wallis test, Simes-Hochberg method ($p < 0.05$).

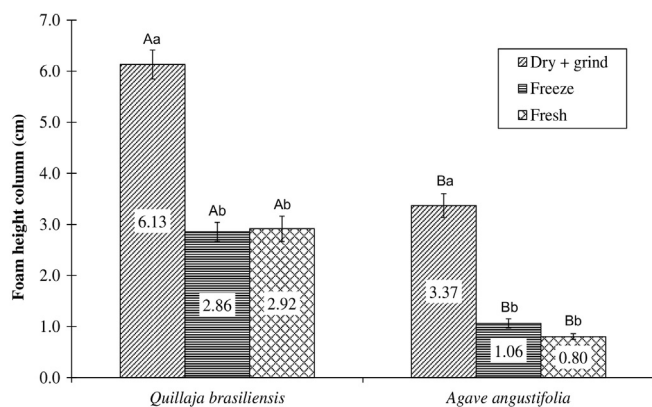


Fig. 1. Average of foam height column (cm) formed by *Quillaja brasiliensis* and *Agave angustifolia* from different methods of preparation in all concentrations, concerning the full decoction undiluted. Different capital letters identify significant differences between species in the same methods of preparation and different lower case letters identify significant differences between methods of preparation in the same species using Kruskal-Wallis test and the averages compared by Simes-Hochberg method ($p < 0.05$). Bars upon the columns indicate the experimental error.

mukorossi aqueous extract (51 mN m^{-1} to 0.4%) (Muntaha and Khan, 2015). However, in the other study, *S. mukorossi*, *Verbascum densiflorum*, *Equisetum arvense*, *Betula pendula* and *Bellis perennis* in 6 h methanol maceration followed by rotation evaporation reached 41.8 , 41.5 , 37.9 , 45.7 and 36.8 mN m^{-1} , respectively (Tmáková et al., 2016). Thus, saponins extraction process, analytical methods and experimental conditions are also factors that must be considered when comparing different studies (Basu et al., 2015; Zdziennicka et al., 2012).

From the analysis of the superficial tension values, it was possible to identify the critical micelle concentration (CMC) only for *Q. brasiliensis* 0.5% and NBS 0.25% (Fig. 5).

CMC is the saturation point of the solution where micelles are formed and superficial tension reaches its lower stable value, regardless of concentration increasing (Janků et al., 2012; Mulligan, 2005; Rizzatti et al., 2009). The *Q. brasiliensis* CMC was higher than NSB CMC as well as in most of other studies. The *S. mukorossi* fruit powder to 2% concentration processed in water (25°C) reached CMC 0.13% with a γ_{CMC} near to 51.5 mN m^{-1} (Muntaha and Khan, 2015). CMC of *S. mukorossi*, *E. arvense* and *B. perennis*, in turn, reached 0.243% , 0.033% and 0.076% , respectively, using methanol as solvent (Tmáková et al., 2016). In industrialized saponins of *Q. saponaria*, *Camellia oleifera* and *Tribulus terrestris*, CMC (γ_{CMC}) were 0.008% (38.2 mN m^{-1}), 0.5% (37.0 mN m^{-1}) and 0.1% (51.8 mN m^{-1}), respectively (Böttcher and Drusch, 2016). This fact highlights once more the importance of the description of the analytical method and saponins source used for comparison.

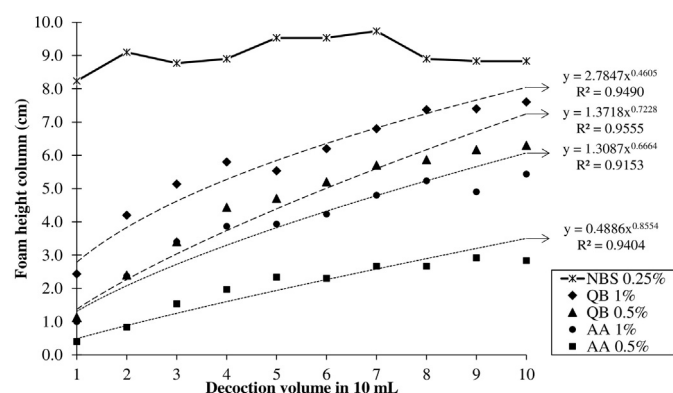


Fig. 2. Average of the foam height column (cm) formed by powder samples of *Quillaja brasiliensis* (QB) and *Agave angustifolia* (AA), at different concentrations and decoction volumes and their respective regression lines compared with neutral bar soap (NBS). Decoction volume 10 represents the full decoction undiluted.

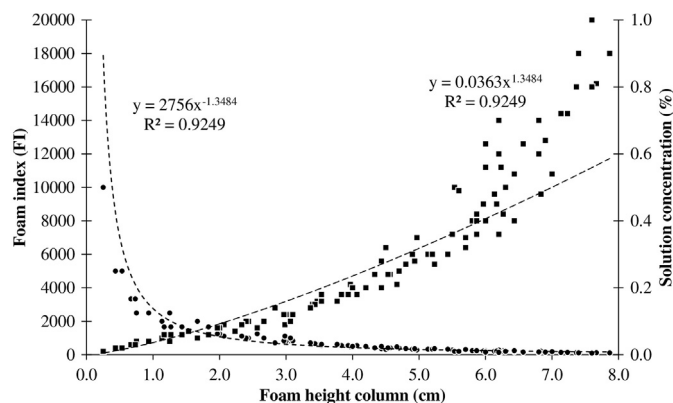


Fig. 3. Foam height column correlation with foam index (FI) and the solution concentration of *Quillaja brasiliensis*, considering all dilutions.

Nevertheless, it is also important to aim that the benefit of *Q. brasiliensis* is not only to reduce the superficial tension, since many studies proved its potential effect for microorganisms and insects controlling (Fischer et al., 2011; de Geyter et al., 2007; Goławska, 2007).

It's worth mentioning that CMC obtained for NBS 0.25% indicates that, in general, its use as surfactant in organic production sprayings has received little attention, since the current recommendations range from 0.5% up to 2% of concentration (Abreu Jr., 1998; Michereff Filho et al., 2013).

4. Conclusion

Drying and grinding methods of preparation showed the best results for the saponins extraction to the both plant species tested. Even so, the fresh or frozen plant methods of preparation can be useful strategies for farmers without drying devices. The *Q. brasiliensis* physical properties were more interesting to use as a natural surfactant than *A. angustifolia*, but was not as efficient as the neutral bar soap (NBS), traditionally used as a surfactant in organic farming. However, more studies should be developed with *Q. brasiliensis*, once its use can play an important role for insects and diseases control in organic farming.

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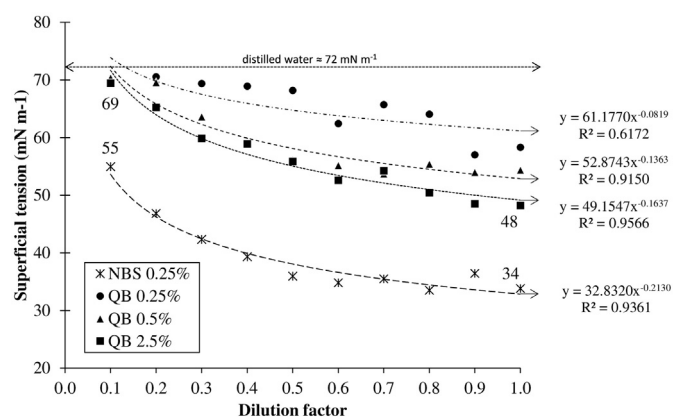


Fig. 4. Regression curves of superficial tension ($\text{mN} \cdot \text{m}^{-1}$) among *Quillaja brasiliensis* (QB) decoctions and neutral bar soap (NBS). Dilution factor 1 represents the full solution undiluted.

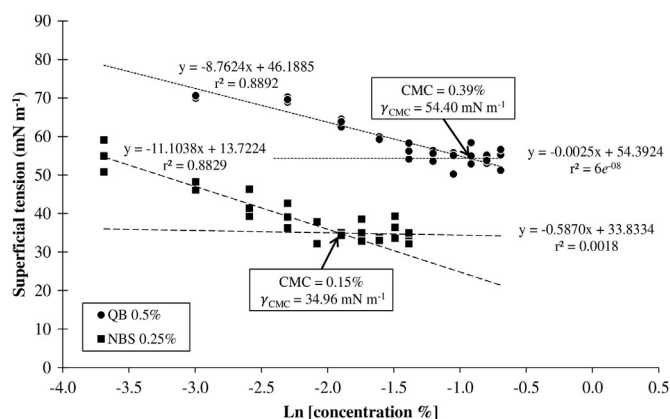


Fig. 5. Critical micellar concentration (CMC) and superficial tension in CMC (γ_{CMC}) of *Quillaja brasiliensis* (QB) 0.5% and neutral bar soap (NBS) 0.25%.

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