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EXPERIMENTAL MEASUREMENTS OF INTERFACIAL TENSION BETWEEN LIQUID-LIQUID MIXTURES IN THE PRESENCE OF SURFACTANTS

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Abstract. *The property interfacial tension between liquid-liquid interfaces is a crucial quantity on the study of emulsion flow rheology and characterization. The use of surfactant molecules on a membrane avoids for instance coalescence of the oil droplets by reducing the interfacial tension of the mixture. A transient effect occurs due to the redistribution of the surfactant molecules at the liquid-liquid interface. The present work carries out interfacial tension measurement as a function of the continuous phase components volume fraction which is equivalent to a liquid-liquid interface of different viscosity ratios. The dependence of the interfacial tension on the volume fraction of surfactants is also examined. The interfacial tension as a function of time is fitted by empirical power-law correlations. The experiments are carried out in a drop volume tensiometer, based on the balance between buoyancy and capillary forces on a drop that is detached from the edge of a capillary tube. The interfacial tension between mineral oil and glycerol/water solution is then measured for several values of glycerol volume fractions. The interfacial tension between oil and water is also measured for various concentrations of Span 80 (lipophilic surfactant) or Tween 80 (hydrophilic surfactant). Again, empirical correlations are proposed in order to fit the experimental data. The equilibrium time and the corresponding equilibrium interfacial tension are used as parameters of the correlations. The results show that the relaxation time for the surfactants distribution reaching steady state decreases with surfactants volume fraction. We determine experimentally the critical value of the surfactant volume fraction and its associated relaxation time. We can expect that beyond the critical concentration, instabilities like drop coalescence could be avoided during the synthesis of an oil-in-water emulsion.*

Keywords: *Interfacial tension, surfactant, emulsion stability, tensiometry, pendent drop method.*

1. INTRODUCTION

Interfacial tension is a fundamental property in fluid-fluid interfaces and emulsions. It has several applications in various fields, such as engineering, medicine and chemistry. For this end accuracy measurements of interface tension of various fluids are required as a function of time, surfactant volume concentration and temperature. The last two quantities produces gradient of surface tension on a interface leading to tangential stress and consequently Marangoni effects. An instructive review on the physics of fluid dynamics involving interfaces between two liquid phases is due to Anderson (1989).

In the first part of the present work, interfacial tension measurements between mineral oil and glycerol/water solutions are carried out for various glycerol volume fractions. Butler (1932) has developed a thermodynamical model in order to predict the interfacial tension σ between two immiscible phases with several components, based on the thermodynamical theory of Gibbs (1906). For an aqueous solution with one solute, the relation is the well known *Sziszkowski Equation* (Szyszkowski, 1908).

In the second part of this work, the effect of surfactants on the interfacial tension between mineral oil and water are examined. In the present context, surfactant are molecules of an appropriate substance (i.e. hydrophobic or hydrophilic) that in a state of low volume concentration on an interface adsorb to this interface where their energy is lower. Therefore, surfactants have an effect of reducing the interface free energy and consequently the interfacial tension. The use of surfactants for synthesis of emulsions avoids the coalescence of oil droplets, which provides a long period of emulsion stability. There is a threshold values for the interfacial tension, when the surfactant concentration reaches a critical value ϕ_c (i.e. *cmc - Critical Micelle Concentration*) (Rosen, 2004). From this point, the interfacial tension remains nearly constant or decays with minimum slope. According to Rosen (2004), the difference between the no-surfactant interfacial tension σ_o and the corresponding value at ϕ_c is called the interfacial pressure $p_{sc} = \sigma_o - \sigma_c$. A surfactant with greater p_{sc} (or lower σ_c) then another surfactant is said to be more effective. The surfactant with lower ϕ_c is said to be more efficient. In other words, a more efficient surfactant gives the same surface pressure with less surfactant but a more

effective surfactant has greater critical value for surface pressure.

The *Gibbs' Adsorption Equation* is a fundamental relation in adsorption processes (Rosen, 2004). Indeed, close to ϕ_c, the interfacial tension and the logarithm of surfactant volume concentration are linearly related by:

$$\Gamma = -\frac{1}{RT}\left(\frac{d\sigma}{d(\ln\phi)}\right) , \tag{1}$$

where R is the constant of surfactant molecule gas, T is the absolute temperature and Γ is the surface excess concentration. The molecular area A_m is given by $A_m = 1/\Gamma N_A$, where N_A is the Avogradro's constant.

In the presence of surfactant interfacial tension shows a time dependence. Actually, there is a transient effect due to the redistribution of surfactant molecules along the interface associated with interfacial tension gradients (i.e. Marangoni's stresses). There is also the adsorption-desorption mechanism between the interface and the bulk phase. The net result is a reduction of the interfacial tension with time, until it reaches an equilibrium state.

Hua and Rosen (1988) have proposed an empirical correlation for the dynamical interfacial tension as a function of time. In a mono-log plot of interfacial tension versus time logarithmic, tree regions are usually identified; I - induction region; II - decay region; III - equilibrium region. The typical correlation is expressed by:

$$\frac{\sigma_o - \sigma}{\sigma - \sigma_e} = \left(\frac{t}{t^*}\right)^n , \tag{2}$$

where σ is the instantaneous interfacial tension, σ_o is the interfacial tension for pure water, σ_e is the equilibrium interfacial tension. Here, n and t^* are empirical parameters for experimental data fitting using equation (2). These correlation is equivalent to Cross correlation, in a context of non-Newtonian fluid dynamics (e.g., Cross (1967)). The equilibrium time t_e is defined as the time for which $\sigma - \sigma_e = (1/10)(\sigma_o - \sigma)$.

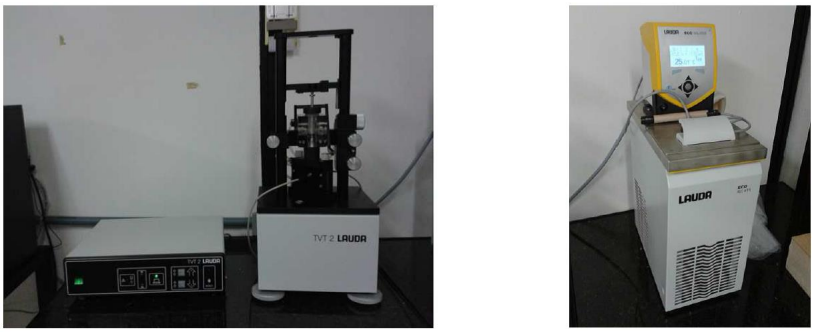
2. MATERIALS AND METHODS

The main apparatus of the experimental setup is a drop volume tensiometer model Lauda TVT available at the Micro-hydrodynamics and Rheology laboratory in University of Brasilia. Figure 1 shows the experimental setup for the interface tension measurements. The surface tension measurement using this tensiometer is based on the method of pendent droplet. In another words, on the simple balance between buoyancy and capillary forces acting on a drop detached at the edge of a capillary tube. The technique allows us to measure surface tension of a liquid interface immersed air, or a interfacial tension between two liquids. In addition, the system gives also support to perform investigations of interfacial tension time-dependence. The measurement approach can be described as follows. Firstly, a syringe of $2.5\ ml$ is filled with one liquid. This liquid must be the one that better wets the capillary edge, and it is usually the more viscous. The other liquid goes in a small crystal cavity of $20\ ml$. A thermal bath is used for a rigorous temperature control of the experiment. Secondly, the capillary edge must be completely immersed in the cavity liquid. A capillary of 1.38 mm radius is appropriate for most measurements. When the interfacial tension is high and the density difference is small the drop becomes to large to be detected. In this case, smaller capillaries should be used. If the syringe liquid is more dense, a straight capillary tube must be used. In case the cavity liquid is more dense, a reverse capillary tube must be used and the drop will formed at the bottom and will arise to the surface. A moving barrier pushes the syringe and the drop is formed. When the droplet reaches a critical volume V, it detaches from the capillary. A optical sensor connected in a light barrier detects the drop and it stops the displacement of the moving barrier. A software calculates the drop volume as the product of the moving barrier displacement and the syringe cross area. The interfacial tension is then calculated based on the equation:

$$\sigma = \frac{Vg\Delta\rho F}{2\pi r_c} , \tag{3}$$

where $\Delta\rho$ is the density difference, r_c is the capillary radius and F is a correction factor. The process of drop generation is repeated at least five times and the mean value and standard deviation are estimated. The tensiometer used has tree measuring modes, from witch two have been used in the present experiment: standard mode and quasi-static mode. Standard mode is used when there is no time dependence of the interfacial tension. This means that the drop formation time is constant for all measurements. The quasi-static mode is used in the presence of surfactants. A drop is formed bellow the critical volume. The interfacial tension decreases with time until the drop detaches. A sequence of drops of decreasing volume is made, so that the formation time increases.

The measurements of interfacial tension between mineral oil and water/glycerol solution are carried out by using the standard mode approach of the tensiometer, because there is no time-dependence. The water/glycerol fills the cavity whereas the mineral oil fills the syringe. Because mineral oil is less dense than water/glycerol solution, oil droplets are formed at the edge of a reverse capillary tube. The water/glycerol solutions are modified by adding volume fractions of glycerol ranging from $\phi = 0$ to 0.7. The glycerol used has density 1.257 and viscosity $868\ cP$ and the mineral oil has density 0.869 and viscosity $137\ cP$. The measurements of interfacial tension in the presence of surfactant are carried



(a) (b)

Figure 1. (a) Tensiometer Lauda TVT 2 and (b) Thermal bath Lauda ECO RE 415.

out using the method of quasi-static mode. The distilled water fills the cavity whereas the mineral oil fills the syringe. Again, the reverse capillary tube is used. Two types of surfactants are investigated. The first surfactant called Span 80 is a lipophilic surfactant added to the mineral oil phase. The second one called Tween 80 is a hydrophilic surfactant added to the water phase. Several surfactant concentrations are investigated during the experiments. The surfactant solutions of very low surfactant concentration are prepared by a sequence of dilutions. In order to guarantee the action of the surfactants on the fluids, the solutions are left at rest at the tensiometer for 10 minutes before experiments.

3. RESULTS AND DISCUSSION

3.1 Interfacial tension of a binary mixture

The interfacial tension on the interface between mineral oil and water/glycerol solution is obtained for ϕ ranging from 0 to 0.7. The plot of Figure 2 shows the variation of the non-dimensional interfacial tension as a function of glycerol volume fraction. Measurements for $\phi > 0.7$ are not performed since the tensiometer is unable to detect the formation of a droplet. Actually, for glycerol volume fractions close to 0.9, the refractive index of water/glycerol solution and mineral oil are too close, so that the oil drop is not visible to the light barrier. Under this condition the interfacial tension for glycerol from ϕ ranging from 0.8 to 1 are just estimated by a simple linear extrapolation. In this plot shown in Figure 2 the data are fitted using *Szyszkowski Equation*:

$$\frac{\sigma}{\sigma_o} = 1 + A\ \ln(1 + B\phi) \tag{4}$$

where σ_o is the interfacial tension for pure water, ϕ is the glycerol volume fraction and A and B are empirical constants. The insert of Figure 2 shows how the refractive index of the aqueous solution of glycerol increases as the volume fraction of glycerol. We can see the matching of the refractive index ($n = 1.46$) of the mineral oil with the water-glycerol solution for a volume fraction of glycerol around 0.9.

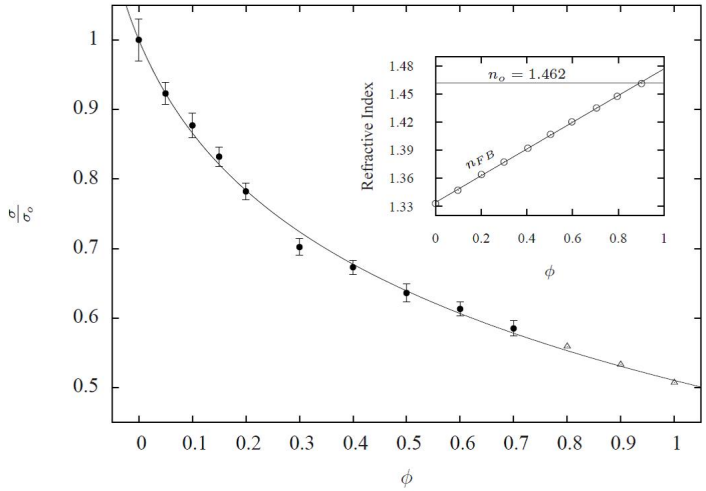


Figure 2. Non-dimensional interfacial tension as a function of the glycerol fraction. Empirical constants: $A = -0.22$, $B = 8.55$.• Experimental data,△Extrapolated values,− Equation (4). *Insert graph*: Refractive Index n_{FB} of a glycerol/water mixture as a function of the glycerol fraction. n_o - Refractive index of mineral oil.○ Data from Assoc. (1963).

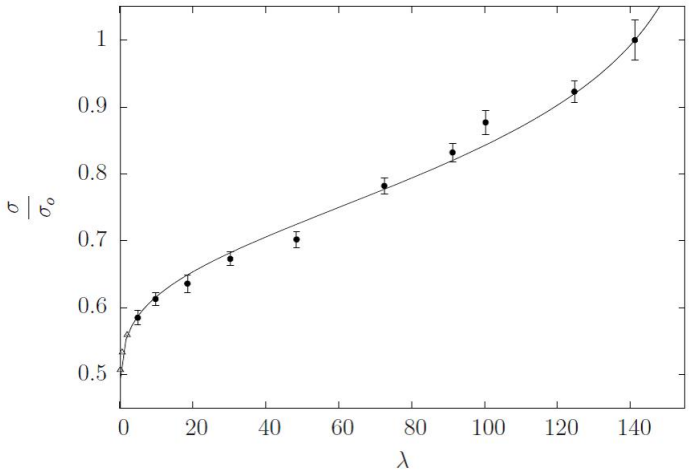


Figure 3. Non-dimensional interfacial tension as a function of the viscosity ratio. Empirical constants are: $A = -0.130$, $B = -6.837$. • Experimental data, △ Extrapolated values,− Equation (5).

Figure 3 shows the plot of the interfacial tension as a function of the viscosity ratio λ between mineral oil and glycerol/water solution. The experimental data behavior have suggested a slight modification in the *Szyszkowski Equation* in order to provide the best fitting of the data. For this end, the variable ϕ is replaced by $\ln(\lambda/\lambda_o)$, with $\lambda_o = 141.2$ being the viscosity ratio between mineral oil and distilled water. Thus, the new best fitting equation is proposed to be:

$$\frac{\sigma}{\sigma_o} = 1 + A\ \ln\left(1 + B\ \ln\left(\frac{\lambda}{\lambda_o}\right)\right) \tag{5}$$

The experimental constants have also been recalculated as indicated in the caption of Figure 3. The empirical model fits very well the experimental data. It should be important to note that the double logarithmic expression is necessary due to the implicit dependence of ϕ with λ. Notice the inflection point at $\lambda = 60.1$.

3.2 Interfacial tension in the presence of surfactants

The interfacial tension between mineral oil and water was measured for various concentrations of Tween 80 and Span 80, used separately. The experimental data are fitted with 6 correlation according to the variation proposed by Hua and Rosen (1988) :

$$\sigma - \sigma_e = \frac{\sigma_o - \sigma_e}{1 + (t/t^*)^n}\ . \tag{6}$$

For each concentration, the equilibrium interfacial tension σ_e and the equilibrium time t_e are estimated. Figures 4 and 5 show monolog plots of the dimensional interfacial tension as a function of time for four different volumes concentrations of Tween 80 and Span 80, respectively. The results in Figures 4 and 5 indicate interfacial tension as a decreasing function of the drop formation time. This behavior is directly related to the unsteady state distribution of surfactant on the drop surface, which is related with the mechanism of desorption and adsorption of surfactants molecules.

For each surfactant examined, the equilibrium interface tension is plotted as a function of surfactant concentration such as depicted in Figures 6 and 7. Typically, we can see from these plots a relative fast decay region followed by a constant region. The intersection of the regions gives the critical micelle concentration ϕ_c. For the fast decay region, interfacial tension decays linearly with the logarithmic of concentration, as predicted by *Gibbs' Adsorption Equation* (Rosen, 2004):

$$\sigma = a\ln(\phi) + b\ , \tag{7}$$

where $a = -11.5\ mN/m$ and $b = -128\ mN/m$, for Tween 80 and $a = -8.4\ mN/m$ and $b = -60\ mN/m$, for Span 80. For very low concentration, however, the logarithmic dependence is no longer valid. At this asymptotic limit a first order linear MacLaurin series fits the data:

$$\sigma = a\phi + b\ , \tag{8}$$

where $a = -2.4 \times 10^7\ mN/m$ and $b = 50.5\ mN/m$, for Tween 80 and $a = -1.55 \times 10^6\ mN/m$ and $b = 50.5\ mN/m$, for Span 80.

For each species of surfactants we have calculated the critical micelle concentration ϕ_c, and the corresponding interfacial tension σ_c, surface pressure p_{sc} and molecular area A_c. The calculations are presented in Table 1.

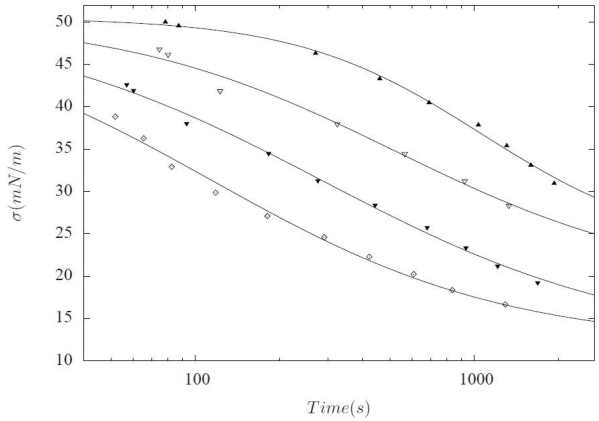


Figure 4. Interfacial tension as a function of drop formation time in the presence of Tween 80. The experiments are carried with constant temperature kept at 25^oC. $-$ Cross Correlation. $\phi = 1.5 \times 10^{-6}$, $\phi = 2.5 \times 10^{-6}$, $\phi = 5 \times 10^{-6}$,$\diamond$ $\phi = 1 \times 10^{-5}$.

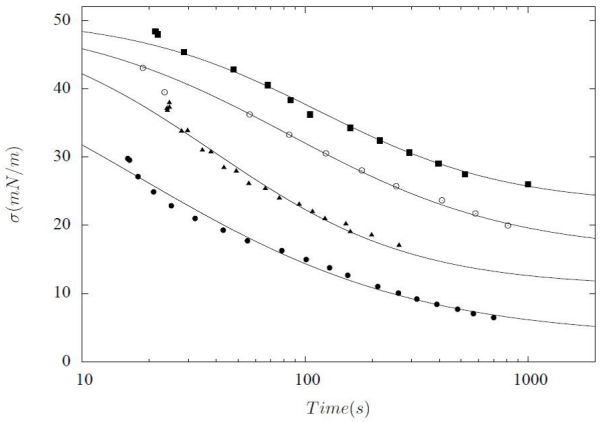


Figure 5. Interfacial tension as a function of drop formation time in the presence of Span 80. The experiments are carried with constant temperature kept at 25^oC. $-$ Cross Correlation. $\phi = 5 \times 10^{-5}$,$\circ$ $\phi = 1 \times 10^{-4}$, $\phi = 2 \times 10^{-4}$,$\bullet$ $\phi = 5 \times 10^{-4}$.

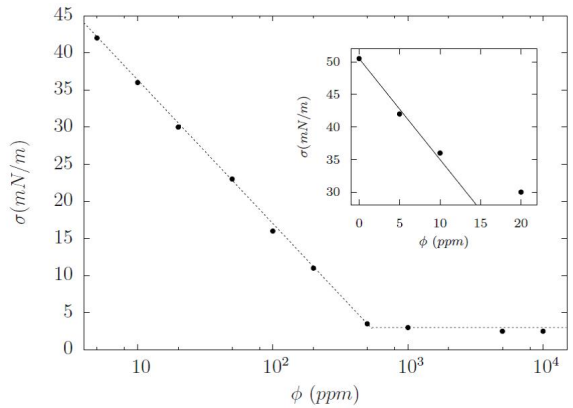


Figure 6. Interfacial tension as a function of Tween 80 concentration - - Equation (7). Insert figure corresponds to interfacial tension at very low concentrations. $-$ Equation (8). The experiments are carried with constant temperature kept at 25^oC. $\bullet$ Tween 80. $\phi_c = 5.0 \times 10^{-6}$.

It is seen from our experiments that ϕ_c for Span 80 is 100 times greater than the value for Tween 80. According to the definition given by Rosen (2004), Tween 80 is more efficient. But the surface pressure for Span 80 is higher, thus it is more effective.

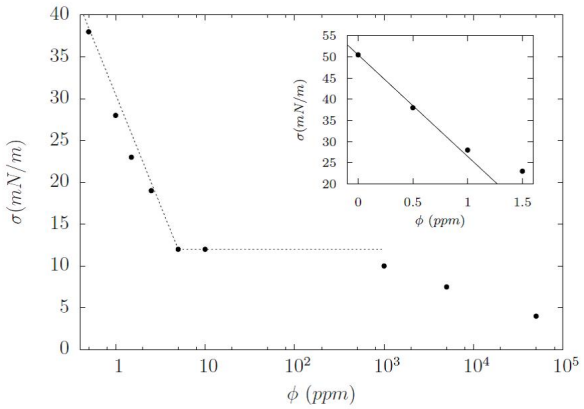


Figure 7. Interfacial tension as a function of Span 80 concentration - - Equation (7). Insert figure corresponds to interfacial tension at very low concentrations. − Equation (8). The experiments are carried with constant temperature kept at 25^oC. • Tween 80. $\phi_c = 5.3 \times 10^{-4}$.

Table 1. Surfactant properties.

	Tween 80	Span 80
ϕ_c (v/v)	5.0×10^{-6}	5.3×10^{-4}
$\sigma_c\ (mN/m)$	12	3
$p_{sc}\ (mN/m)$	38.5	47.5
$A_c\ (10^{-20}m^2)$	36	49

The equilibrium time decreases with the surfactant concentration, as shown in Figure 8, until it reduces to a few minutes at high concentrations. Again, experimental data is very well fitted by an empirical Sisko correlation

$$t_e = t_\infty + C\phi^{n-1}\ , \tag{9}$$

expect at the asymptotic regime of very low concentrations where a spreading of the data is observed. Here t_∞ is the equilibrium time for $\phi \to \infty$ and C and n are fitting empirical constants. For Span 80, $t_\infty = 30\ s$, $C = 0.0081\ s$ and $n = -0.2$. For Tween 80, $t_\infty = 100\ s$, $C = 0.0006\ s$ and $n = -0.3$.

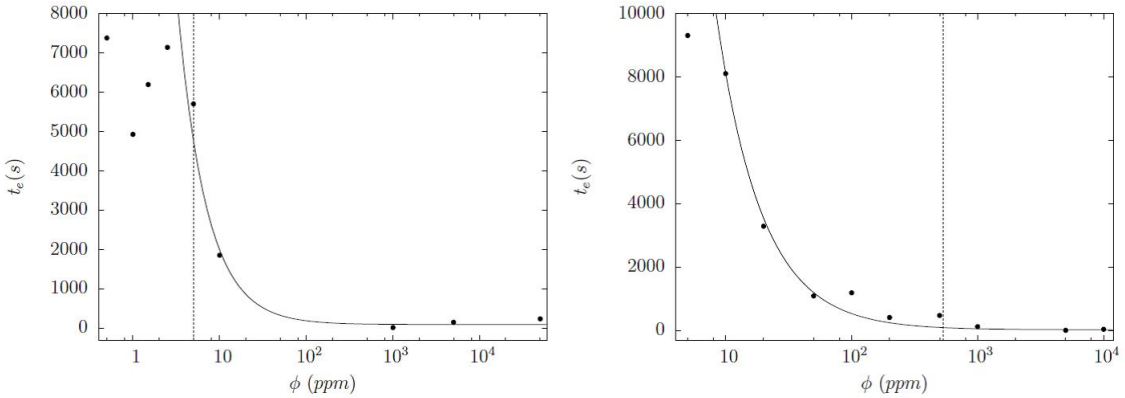


Figure 8. Equilibrium time as a function of (a) Tween 80, (b) Span 80 concentration. The experiments are carried with constant temperature kept at 25^oC. • Experimental data. − Equation (9). - - Tween 80 : $\phi_c = 5.0 \times 10^{-6}$. Span 80 : $\phi_c = 5.3 \times 10^{-4}$

For very low concentration there is substantial spreading of points because the liquids in the presence o surfactants are very unstable at this values of volume fractions. Equilibrium time at ϕ_c for Tween 80 is high ($5000\ s$) compared to Span 80 ($500\ s$). In the investigations on surfactants action, the interest region is close to ϕ_c. For this end, Span 80 is more appropriate because the equilibrium time is compatible with the drop volume formed on the tensiometer, which measures from 20 to 3600 s.

4. CONCLUSIONS

Interfacial tension between mineral oil and glycerol/water solution has been described very well by *Szyszkowski Equation* for the glycerol volume fraction and the modified equation for the viscosity ratio. In the presence of surfactants, interfacial tension showed a clear dependence on time, that is confirmed by typical correlation function describing very well the experimental data. High concentration solutions reached equilibrium faster. For the synthesis of emulsions, this work suggests that the Tween 80 concentration should be at least 100 times the ϕ_c and for Span 80 at least 10 times the ϕ_c. Also, emulsion samples should rest at least 10 minutes before its rheological characterization. Equilibrium interfacial tension decreased with the logarithmic of concentration, below ϕ_c, as predicted by *Gibbs' Adsorption Equation*, except for very low concentrations, which was described by a linear relation, and concentrations after ϕ_c, for which the interfacial tension is almost constant.

5. ACKNOWLEDGEMENTS

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