

Influence of Glycerides–Xanthan Gum Synergy on Their Performance as Lubricants for Water-Based Drilling Fluids

Denise Gentili Nunes,¹ Andréia de P.M. da Silva,¹ João Cajaiba,¹ Aurora Pérez-Gramatges,² Elizabeth Roditi Lachter,¹ Regina Sandra Veiga Nascimento¹

¹Universidade Federal do Rio de Janeiro (UFRJ), Instituto de Química, Pólo de Xistoquímica, Rua Hélio de Almeida 40, Cidade Universitária RJ, Brazil

²Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro 22453-900, Brazil

Correspondence to: R. S. V. Nascimento (E-mail: rsandra@iq.ufrj.br)

ABSTRACT: Water-based fluids for drilling wells are an environmentally friendly alternative to oil-based formulations typically used in the oil industry. Aqueous mixtures of nonionic monoglyceride surfactants (C6, C8, C10, C12, and C18 carbon chains) and xanthan gum (XG) were investigated with that purpose, correlating their lubricity and solubility in water, as well as using surface tension and contact angle measurements. The results showed that monoglycerides behave as excellent lubricants in water, with a steady decrease of the friction coefficient as the hydrocarbon chain length increased. Monoglycerides were able to reduce the friction coefficient even further when used in XG suspensions, suggesting that they are probably forming a complex with the polysaccharide that shows a synergy toward their performance as lubricants. Experiments of adsorption onto iron oxide nanoparticles also produced evidence of the interaction between these molecules, which favors their adsorption on the metal surface. These results indicate that interactions occurring in solution between the surfactants and the polysaccharide are crucial in the mechanism of action of these mixtures as lubricants in water-based drilling fluids. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41085.

KEYWORDS: adsorption; friction; oil and gas; wear and lubrication

Received 27 March 2014; accepted 27 May 2014

DOI: 10.1002/app.41085

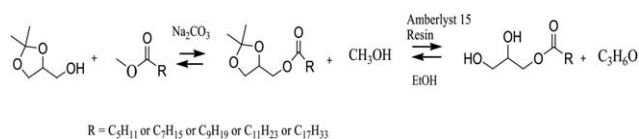
INTRODUCTION

Lubrication technology has been drawing a lot of attention in the last decades, and among the most important new products are the water-based lubricants, which have been developed mainly due to their ecological advantages, biodegradability, and low toxicity.¹ Water-based lubricants have been used in many industrial fields such as in metal working processes, biological systems, and drilling fluids.^{1,2} The drilling fluids have an extremely important role in the drilling process of an oil well, where the fluid is circulated continuously during the entire process and the type of fluid to be used depends on the type of rock being drilled and the trajectory of the well. One of the major challenges in drilling fluids technology comes from the use of water-based fluids for drilling wells that require higher lubricity, such as in directional wells.^{3–5} While oil-based fluids present a naturally low friction coefficient (FC),⁶ water-based fluids need lubricant additives that would be able to reduce the frictional resistance.

Commercial liquid lubricants for water-based drilling fluids can include different types of chemicals such as glycols, glycerides,

fatty acids, esters, phosphates, poly(ethylene glycol) derivatives, and surfactants.^{7,8} It is believed that those systems should be able to form a film strongly attached to the surfaces to be lubricated, and for that adhesion, lubricants should present polar groups, for example, hydroxyls, in their chemical structures.^{9,10} Reports from the literature also mention the importance of the presence of hydrophobic segments, such as alkyl groups, in the structure of the lubricant.^{10,11} Therefore, an efficient lubricant for water-based systems should have a chemical structure similar to that of surfactants, with an amphiphilic structure presenting hydrophilic heads and hydrophobic tails.^{11,12}

Monoglycerides are molecules that exhibit an amphiphilic structure, with polar and nonpolar segments.^{13,14} These compounds are classified as nonionic surfactants, and are widely used in pharmaceutical, food, and cosmetics industries as emulsifiers, emollients, and also lubricants for aqueous systems.^{9,15} According to Boschkova,¹⁶ the hydrophilic heads of monoglycerides will adsorb on the metal surface, and the alignment and aggregation of the surfactant molecules will form monolayers of multi (liquid crystalline) layers, leading to a good boundary



Scheme 1. Transesterification reaction of fatty acid methyl esters with 1,2-O-isopropylidene glycerol (solketal) and the deprotection reaction.

film formation and improving lubricity. Sonmez et al.⁸ tested three different types of chemical commercial lubricants in water-based drilling fluids formulations, which are glyceride, triglyceride, and glycol based. The glyceride-based lubricant showed the best performance, but it was not discussed which chemical characteristics led to the better performance of the lubricant. It has also been mentioned in the literature that lubricants for water-based drilling fluids should present low water solubility.¹³ However, the effect and the importance of the water solubility of lubricants on the performance of these fluids have not been properly discussed in the relevant works of the field.

Preliminary studies performed in our laboratories have shown that lubricants with surfactant-like chemical structures presented a much better performance when in the presence of polysaccharides.¹⁷ Xanthan gum (XG) was chosen for this study because it is often used as a rheology modifier for water-based drilling fluid formulations.¹⁸ We believe that the solubility of a lubricant in the aqueous medium can strongly affect its performance, since the lubricant molecules will continuously adsorb and desorb from the metal surfaces when in contact with water.^{9,10} There is a great interest on polymer/surfactant systems due to their physicochemical properties at different possible combinations, forming complexes from the occurrence of strong interactions between their polar sites.^{19–22} The formation of a monoglyceride–polysaccharide complex would probably help to disperse the less-soluble surfactants in the aqueous medium, making possible for them to act as lubricants.²² Therefore, the lubrication mechanism of aqueous solutions can be very complex, and it is not well known yet.

The main objective of this work is to study the synergy between modified glycerides and xanthan gum toward better lubrication performance in water-based fluids, thus contributing to a better understanding of the mechanisms involved in the lubrication of metal parts by surfactant–polysaccharide systems. We chose a series of glyceride surfactants, since their structures would allow for a systematic change in their water solubility. The synthesized surfactants were evaluated by adsorption, surface tension, and wettability measurements, and the results were correlated with the lubricity performance.

EXPERIMENTAL

Materials

Hexanoic, octanoic, decanoic, lauric, oleic, and p-toluenesulfonic (PTSA) acids, as well as the solvents and other reagents (CHCl₃, NaOH, NaCl, Na₂CO₃, ethanol, isopropanol, and ether), were acquired from VETEC SA (Brazil), being all of analytical grade. Methyl hexanoate, octanoate, decanoate, laurate, and oleate esters; 1,2-isopropylidene-glycerol (solketal); Amberlyst 15 wet, and iron oxide (II, III) nanoparticles (*d* < 50 nm), were acquired from Sigma-Aldrich (Brazil). Tetrahydrofuran (THF) and CDCl₃

were purchased from Tedia of Brazil. Commercial lubricant DP400 (lubricant frequently utilized by the oil industry for the formulation of water-based drilling fluids) was acquired from Dhaymers (Brazil). XG was a courtesy from CENPES/PETROBRAS. All reagents were used as received.

Monoglyceride Synthesis

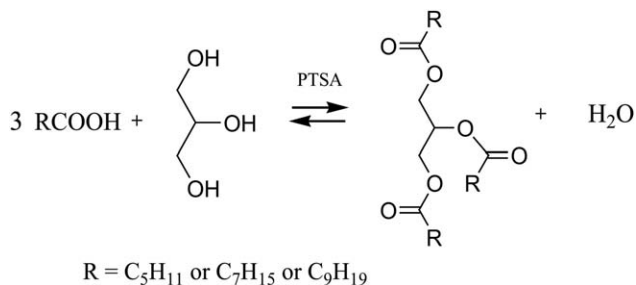
In order to reduce costs, the monoglycerides could be obtained from the esterification reaction between fatty acids and glycerol. However, this reaction produces a mixture of mono, di, and triglycerides, depending on the ratio of reagents. On the other side, it would be important to obtain exclusively monoglycerides, to be able to evaluate the effect of the number of hydroxyls present in the lubricant structure on the lubricant performance. For that purpose, a commercial protected glycerol, solketal, was used in the synthesis, as shown in Scheme 1.

The production of monoglycerides with 6, 8, 10, and 12 carbon atoms chains (C₆, C₈, C₁₀, and C₁₂), and one with 18 carbons and one unsaturation (C₁₈ : 1), were prepared by a transesterification reaction procedure described by Yu et al.,²³ modifying the first reaction step at a temperature of 180°C, reaction time of 5 h, and a solketal : methyl ester molar ratio equal of 3 : 1. The transesterification reaction that leads exclusively to monoglycerides is shown in Scheme 1. Fourier transform infrared spectroscopy (FTIR) spectra of reaction products were obtained with a NICOLET Magna-IR 760 and ¹³C NMR spectra with a BRUKER DRX-200 (50 MHz for ¹³C).

The monoglycerides synthesized differ from each other in the hydrocarbon segment size and are identified by the following nomenclature: glycerol monoesters or monoglycerides were called MonoC_x, where *x* is the number of carbon atoms in the hydrocarbon segment.

Triglycerides Synthesis

The triglycerides with C₆, C₈, and C₁₀ alkyl chains were prepared by esterification reaction. The fatty acid (C₆, C₈, and C₁₀) and glycerol with molar ratio 5 : 1 were mixed with PTSA catalyst, at 2 wt % in relation to the acid mass, and the mixture was submitted to vigorous stirring. The reaction was performed at 130°C in inert atmosphere by bubbling nitrogen gas into the reaction mixture, in an oil bath. After 5 h, the content of the reactor was repeatedly washed with ethanol, chloroform and NaOH 10 wt % solution, for the purification step. The organic phase was evaporated, and the triglycerides obtained were characterized by ¹³C NMR and FTIR. The esterification reaction to obtain the triglycerides is shown in Scheme 2.



Scheme 2. Esterification reaction of fatty acids with glycerol.

The triglycerides synthesized differ from each other in the hydrocarbon segment size and are identified by the following nomenclature: glycerol triesters or triglycerides were called TriCx, where *x* is the number of carbon atoms in the alkyl segment. The TriC12 and TriC18 : 1 obtained were difficult to purify, therefore were not used in the study.

Lubricity Measurements

Monoglycerides (C6, C8, C10, C12, and C18:1) in aqueous solutions and XG suspensions were prepared at 0.25, 0.5, 1.0, 1.5, 2.0, and 3.0 wt % concentrations, and the FC of these systems was measured. The monoglycerides, triglycerides (C6, C8, and C10), and the commercial lubricant DP400 aqueous solutions were added to a 0.43 wt % (1.5 lb/bbl) water suspension of XG (XG) and after 5 min of mixing at 16,000 rpm, the lubricity of the systems was measured. All solutions were prepared at pH 9–10, since drilling fluids are always formulated at alkaline pH. Lubricity measurements were performed in a Fann Lubricity Tester Model 21200 equipment. The test is performed applying a 150 N force to a system comprising a block and a ring spinner kept at 60 rpm. The ring-block friction system is immersed in a vessel containing the fluid to be evaluated, and simulates a metal-metal type of friction, measuring the torque that is directly related to the value of the FC in a boundary lubrication regime. The apparatus was previously calibrated with distilled water, of FC 0.34.

Solubility Measurements

The water solubility experiments were performed in a glass reactor of 0.1-L capacity, Easy-Max Mettler Toledo model, coupled to a FTIR with a probe for attenuated total reflectance (ATR). Fifty milliliters of water were added to the Easy-Max reaction vessel, and successive additions of monoglycerides (C6, C8, C10, and C12 and C18 : 1) were made. Temperature was maintained at $25 \pm 0.1^\circ\text{C}$, and the stirring rate was kept at 200 rpm. The infrared probe identifies only the component that is in solution, and the solubility is measured at the maximum absorption signal obtained. The lubricant solubilization in water was monitored by the change in the size of the carbonyl band signal ($1750\text{--}1600\text{ cm}^{-1}$) after each lubricant addition. After each addition, the new absorption signal is compared with the previous one. This technique is frequently used for characterization of substances and monitoring chemical reactions.²² However, only few citations are found in the literature using ATR-FTIR spectroscopy for the measurement of solubility.^{24,25}

Surface Tension Measurements

Surface tension (γ) measurements were performed with a tensiometer K12 (KRUSS GmbH, Germany) using the Du Nouy ring method, with an instrumental error of 0.1 m N m^{-1} . All measurements were done at 25°C . Surface tension measurements were used to determine interfacial properties and critical micellar concentration (CMC) values of C6, C8, and C10 monoglycerides in aqueous solutions (the other compounds were not sufficiently soluble in water). The surfactant was progressively added to either water or an aqueous suspension containing XG at pH 9–10. Since the addition of the polysaccharide considerably increases the viscosity of the solution, making more difficult and unreliable the surface tension measurements, the XG

concentration was adjusted to the maximum possible value (0.15 wt %). The mixture was stirred for 3 min, and left to rest for another 5 min before the measurement. The CMC values for surfactant alone and in the presence of the polysaccharide were estimated as the breakpoints in the γ vs $\log C_{\text{surf}}$ plot.

Contact Angle Measurements

Contact angle measurements were performed using an automatic goniometer (Data Physics, model SCA-20) and the ellipse fitting method. Lubricant solutions of C6, C8, and C10 monoglycerides (1.0 wt %), in water and in 0.15 wt % XG suspensions at pH 9.0, were dispensed as drops on a polished metal surface, using a syringe ($d = 1.65\text{ mm}$). The contact angle was then measured as a function of time, during 1 min. The XG concentration used was 0.15 wt % because, above this value, high viscosity of the solutions can hinder contact angle measurements.

Adsorption Measurements

Adsorption measurements of lubricants in aqueous solutions on iron oxide nanoparticles surfaces, at the concentration range from 0.05 to 5 wt %, were only possible for C6, C8, C10, and C12 monoglycerides, since C18 is not sufficiently soluble in pure water. Monoglycerides (C6, C8, C10, C12) and the triglyceride C10 water systems, at the same concentrations as above, were added to a 0.43 wt % XG aqueous suspension. To each system, 1 g of iron oxide nanoparticles was also added. Aqueous suspensions of XG at known concentrations (in a range from 0.2 to 2 wt %), and iron oxide nanoparticles systems, were also analyzed. All systems were prepared at pH 9–10. The iron oxide/lubricant and the iron oxide/lubricant/XG suspensions were shaken in a water bath at 25°C for 2 h. Afterward, the suspensions were centrifuged at 3500 rpm and washed twice with Milli-Q water. The solids were oven-dried at 100°C , and the adsorption was quantified by elemental (CHN) analysis, using a Thermo Finnigan apparatus (FlashEA 1112).

RESULTS AND DISCUSSION

Monoglycerides and Triglycerides Characterization

The structure of the monoglycerides and triglycerides synthesized was confirmed through FTIR and ^{13}C NMR analysis. The ^{13}C chemical shifts (δ) in CDCl_3 relative to tetramethylsilane (TMS) were quite similar for the different esters: $\delta = 174.5\text{ ppm}$ (RCOOR') for the monoglycerides and $\delta = 62\text{ ppm}$ (C-1(3), CH_2O) and $\delta = 69\text{ ppm}$ (C-2, CHO) for the triglycerides. The FTIR spectra showed characteristic peaks at 3411 cm^{-1} (OH) and at 1740 cm^{-1} ($\text{C}=\text{O}$) for the monoglycerides, and only at 1740 cm^{-1} ($\text{C}=\text{O}$) for the triglycerides.

Lubricity Measurements

The FC for the monoglycerides in water solutions and in XG suspensions at different lubricant concentrations are shown in Figure 1(a–e). The FC measurements for XG suspensions at several concentrations were also performed, and the results are shown in the same figure. The results show that the XG alone is not able to promote lubricity.

Figure 1(a) shows that monohexanoate of glycerol, either in water or in the XG suspension, is not able to reduce significantly the FC of the systems. However, all the other

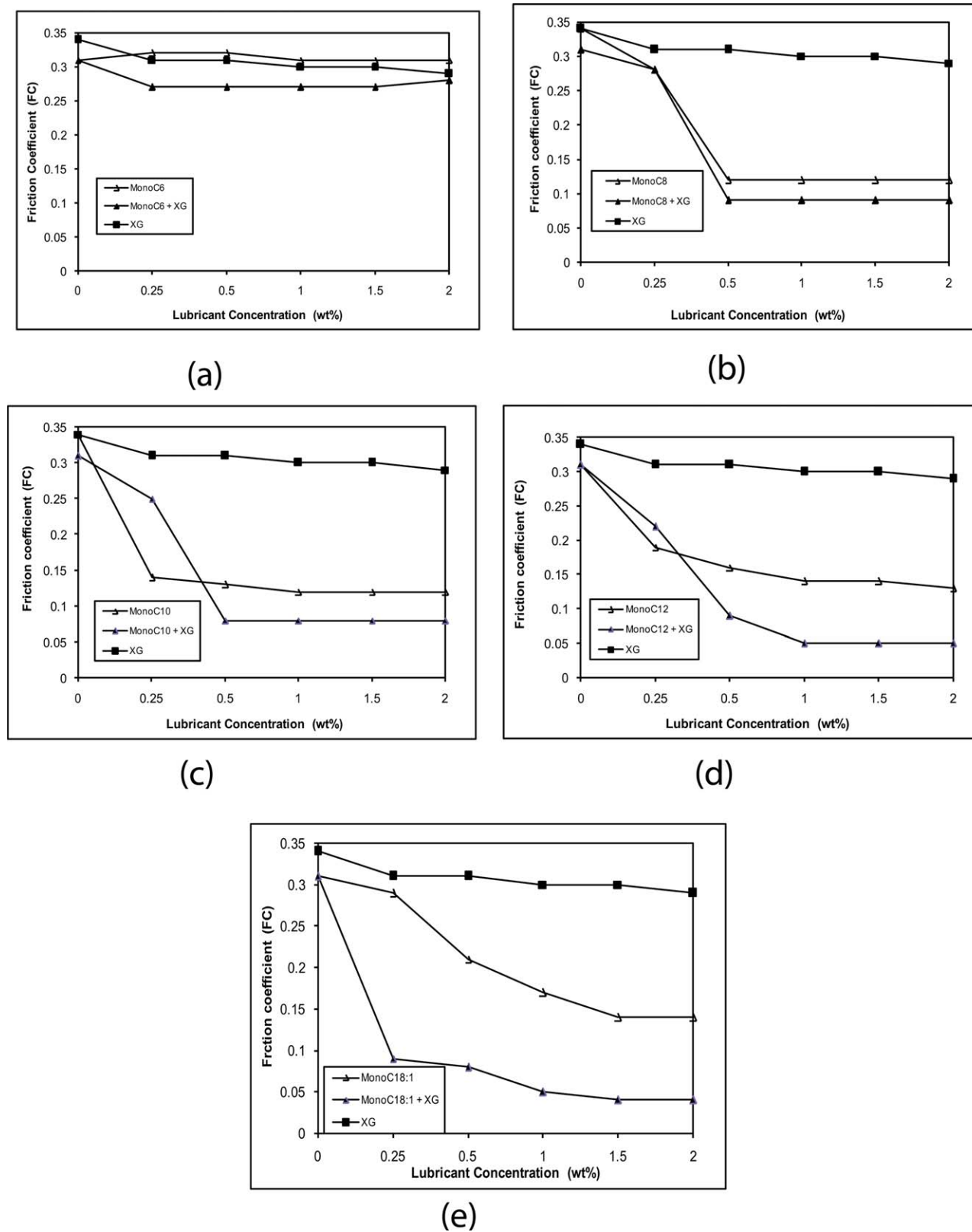


Figure 1. FC for XG suspension, monoglycerides in water solutions and in 0.43 wt % XG suspension as a function of lubricant concentration. (a) MonoC6, (b) MonoC8, (c) MonoC10, (d) MonoC12, and (e) MonoC18:1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Friction Coefficient for Monoglycerides, Triglycerides, and DP400 (2 wt %), in 0.43 wt % XG Suspension

Monoglycerides	FC	Triglycerides	FC	Commercial	FC
MonoC6	0.28	TriC6	0.31	DP400	0.15
MonoC8	0.09	TriC8	0.28		
MonoC10	0.08	TriC10	0.28		
MonoC12	0.05	-			
MonoC18:1	0.04	-			

monoglycerides reduce drastically the FC in water, when in concentrations above 0.5 wt %. The results also show that these monoglycerides reduce the FC even further when in the XG suspension, suggesting that they are probably forming a complex with the polysaccharide, leading to a synergistic effect. This decrease of the FC is also much more significant for the monoglycerides with longer alkyl chains (C12 and C18 components of the series) than for those with shorter alkyl chains.

The FC for all the monoglycerides and triglycerides, as well as for the commercial product DP 400, at a concentration of 2 wt % are shown in Table I.

According to these results, all the monoglycerides with hydrocarbon chains longer than C6 are excellent lubricants when in the presence of XG, being able to decrease the FC of water from 0.34 to values lower than that of the commercial lubricant DP400 (0.15). The monooleate of glycerol (MonoC18:1) presented the best performance, with an FC of 0.04, which is even lower than that shown by oil-based drilling fluids (0.05).⁶ The order of efficiency found for the monoesters lubricants synthesized in the present work was C18: 1 > C12 > C10 > C8 > C6. The results also show that the triglycerides are not able to reduce the water FC, probably due to the absence of hydroxyl groups in their structure that would prevent the film formation at the metal surface. Other works from the literature have also shown the importance of the presence of OH groups in the glyceride molecular structure.^{10,13}

Solubility Measurements

In order to evaluate the effect of the glycerides solubility in water on their lubricating performance, the solubility of glycerides was measured using FTIR-ATR spectroscopy.

The solubility measurements were performed analyzing the carbonyl signal, which increases with the solubilization of the lubricant until the saturation point of the lubricant in the aqueous solution is reached, and the signal becomes constant. Figure 2 shows the saturation point for the monohexanoate of glycerol in water, at the point where the carbonyl signal becomes constant, for example, when the area of the C=O band reaches 6.3 absorbance units (A.U.).

It was not possible to measure the solubility of the monooleate of glycerol, due to the fact that its water solubility is lower than the detection limit of the equipment. All the other monoglycerides (C6–C12) had their solubility in water quantified. To analyze the ester concentration in the aqueous medium, a calibration curve for the carbonyl absorption ($1750\text{--}1600\text{ cm}^{-1}$) was constructed for each monoglyceride. They relate the mass

of lubricant in solution to the absorption band area for the carbonyl during the dissolution process of the lubricant in water at 25°C, before reaching the saturation point. All the analyzed lubricants presented a calibration curve, at low concentrations, whose quadratic correlation coefficient was higher than 0.99, indicating a good linear relationship with the mass of lubricant added. The equilibrium concentration of the lubricant in solution was obtained by measuring the mass of lubricant which saturates the system, and it was calculated from the area of the carbonyl band as a function of the mass of lubricant. The mass of lubricant that saturated the system was calculated from the respective calibration curves. The saturated mass is the point on the curve where the area becomes constant minus the linear coefficient found. This value is divided by the angular coefficient to obtain the saturated mass. The values found were 5.76, 1.56, 1.26, and 0.49 g for the C6, C8, C10, and C12 monoesters, respectively. These masses were solubilized in 50 mL of water so 11.5, 3.1, 2.5, and 0.98 wt % are the C6, C8, C10, and C12 lubricants solubilities in water. As expected, the solubility decreases with increasing hydrocarbon chain size.

The results of monoglycerides solubility in water contributed to a better understanding of its effect on the lubricants performance. For the monoglycerides with C8, C10, C12, and C18 carbon chains, there is a steady decrease of the FC with the increase of the hydrocarbon chain length. However, the C6 derivative presents a much higher FC than it would be expected for a difference of just two carbon atoms in the chain, as compared with the C8 monoglyceride result. This finding can be explained by the results of lubricants maximum masses solubilized in water, where C6 presents a much higher solubility in water than the other monoglycerides, indicating that six carbon atoms would be a critical chain length. It can be noticed that there is a direct correlation of FC and water solubility for C6, C8, C10, and C12 monoesters (Figure 3). These results led us to conclude that the FC is highly dependent on the solubility of the lubricant in the aqueous medium, and the dependence on the hydrocarbon chain length is a consequence of the fact that increasing the chain length decreases the solubility. Our results are in agreement with the literature that shows that the

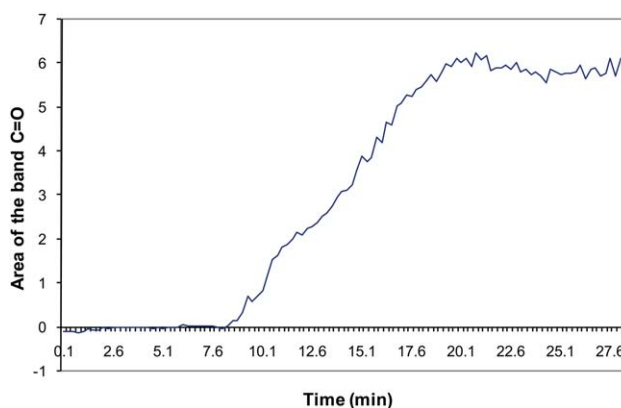


Figure 2. Dependence of the absorption band area for the C=O group at $1750\text{--}1600\text{ cm}^{-1}$ with the time for solubilization of monohexanoate of glycerol in water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

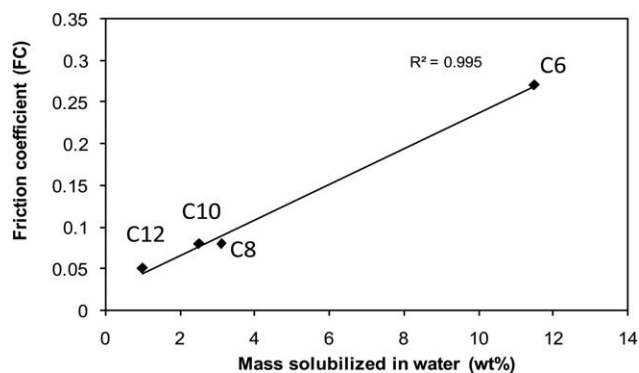


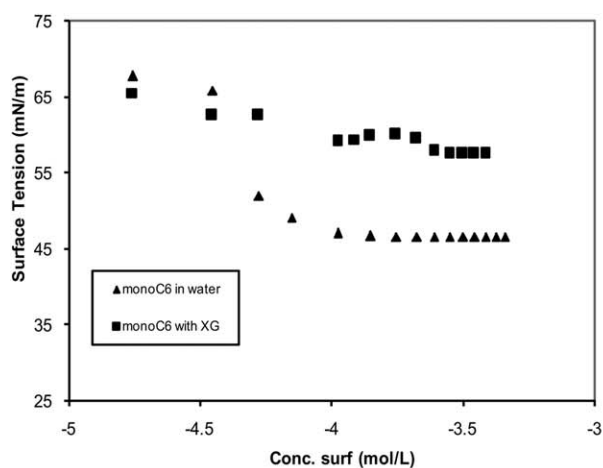
Figure 3. FC as a function of mass of monoglycerides solubilized in water.

lubrication effectiveness depends on the molecular chain length of the lubricant. However, none of those reports do relate their findings with the water solubility of the lubricants.^{10,26}

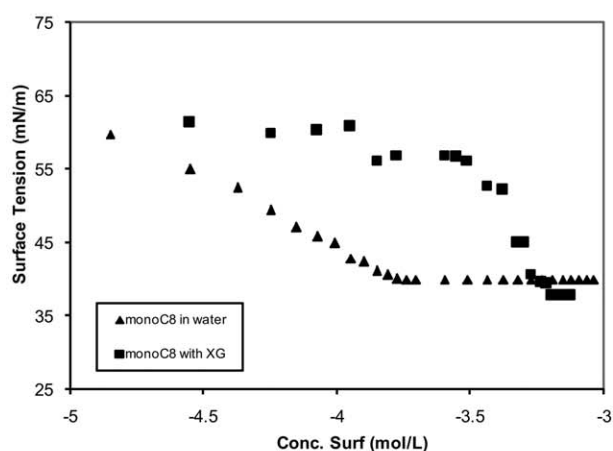
Surface Tension Measurements

Several techniques have been used in the literature to evaluate surfactant–polysaccharides complex formation.^{27–31} In this work, we chose surface tension measurements to study the C6, C8, and C10 monoglycerides-XG system. The C12 and C18 monoglycerides were not sufficiently soluble for the measurements.

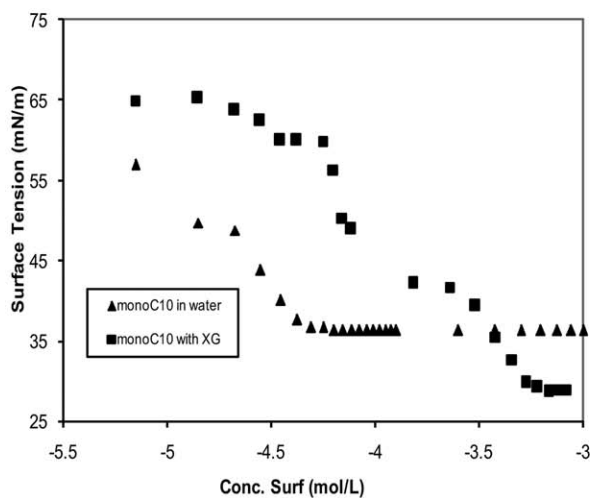
Surface tension (γ) isotherms of C6, C8, and C10 monoglyceride aqueous solutions showed the typical surfactant behavior, with an initial decrease in surface tension and a further stabilization, once the CMC is reached [Figure 4(a–c)]. It is interesting to note that the lower γ values, corresponding to concentrations above CMC, decrease as the hydrocarbon chain increases in the monoglyceride, that is, γ_{CMC} (C6) > γ_{CMC} (C8) > γ_{CMC} (C10). This can be explained based on the consequent increase in hydrophobicity in the surfactant molecule,



(a)



(b)



(c)

Figure 4. Surface tension of surfactant aqueous solutions in the absence and in the presence of XG (0.15 wt %). (a) MonoC6, (b) MonoC8, and (c) MonoC10.

Table II. Critical Micellar Concentrations (CMC) and Surface Tension (γ) Values at CMC of Monoglycerides in the Absence and in the Presence of 0.15 wt % XG

Monoglycerides	CMC in water (M)	γ_{CMC} (mN/m)	CMC in XG (M)	γ_{CMC} (mN/m)
MonoC6	1.74×10^{-4}	46.6	2.79×10^{-4}	57.5
MonoC8	1.70×10^{-4}	40.1	6.4×10^{-4}	37.8
MonoC10	0.63×10^{-4}	36.3	6.8×10^{-4}	28.6

leading to a higher surface activity. Accordingly, the CMC values follow the same trend, since more hydrophobic molecules will aggregate at lower concentrations in aqueous solutions (Table II).

Conversely, the surface tension isotherms in the presence of XG showed a marked difference, compared to the pure aqueous surfactant solutions [Figure 4(a–c)]. While for C6 monoglyceride, the surface tension is barely modified, the profiles are greatly affected for C8 and C10 monoglycerides. This behavior resembles well typical profiles for strongly interacting polymer : surfactant mixtures,¹⁹ which suggests the formation of monoglyceride : xanthan gum complexes both at the interface and in solution. The low final values in surface tension (γ_{CMC}), close to those of the surfactant, also confirm this hypothesis. In addition, the CMC values in the presence of the polysaccharide are shifted to higher concentrations in the C8 and C10 systems, while in the C6 mixture it remains almost unaltered. The shift in CMC is more pronounced in the case of monodecanoate of glycerol, showing a decrease in one order of magnitude (Table II).

Contact Angle Measurements

The contact angle measurements for the lubricants at 1.0 wt % in water are shown in Table III. The contact angle for pure water was 79.8°, used as a reference value since pure water is considered to have no affinity for the metal surface. The results showed that the aqueous solutions of C8 and C10 monoglycerides have a greater affinity (smaller contact angles) for the metal surface than that of C6 monoglyceride. The monohexanoate of glycerol is very soluble in water so its affinity for the aqueous medium would be greater than for the metal surface.

This behavior was confirmed in the results obtained using XG suspensions of the monoglycerides. While the polysaccharide alone produced only a slight decrease of the contact angle (compared to the one of water), the complexes between XG and the longer-chain monoglycerides were able to reduce it to values below 10, showing an excellent interaction of the monoglyceride–XG complex with the metal surface. Similarly to the results

Table III. Contact Angle Measurements of Monoglycerides in Water and in XG Suspensions

Aqueous solutions	Contact angle (°)	XG suspensions	Contact angle (°)
Water	77.0	XG	69.3
MonoC6	64.5	MonoC6+XG	63.7
MonoC8	13.7	MonoC8+XG	9.6
MonoC10	12.9	MonoC10+XG	7.4

in water, the MonoC6/XG suspension was not able to reduce the contact angle, largely remaining in solution.

Adsorption Measurements

The carbon masses corresponding to the mass of glycerides adsorbed from water solutions and XG suspensions onto the iron oxide nanoparticles (wt %) were converted into mols, and adsorption curves were constructed [Figure 5(a,b)].

The results shown in Figure 5(a) indicate that the affinity of the water soluble lubricants for the metal surface increases with the size of the hydrocarbon chain of the additive. As expected, the adsorption of MonoC6 from water solution was extremely low, mainly if compared with the results from the higher hydrocarbon chain monoglycerides. This is probably due to its very high water solubility, which favors desorption from the iron surface. This low degree of adsorption is probably responsible for its low performance as a lubricant, as was seen in the lubricity results (Table I).

The adsorption curves in Figure 5(a,b) allow a comparison between the adsorption behavior between aqueous and XG systems, showing that the C8 and C10 monoglycerides present a similar behavior in both media. These results are in agreement with the lubricity results, where these two glycerides have shown similar behavior, mainly at concentrations higher than 0.25 wt %. These results also show that at 2.0 wt % concentration both glycerides have reached the curves plateau in either media. Conversely, MonoC12, which has a very low solubility in water, presents a completely different behavior in the XG suspension, as compared with the MonoC8 and MonoC10, since it continues to adsorb on the metal surface, even at much higher concentrations. These results indicate that XG has a crucial effect on the C12 glyceride water dispersion, which probably determines its performance as a lubricant. The XG : C12 complex formed would be more hydrophilic than the MonoC12 alone, allowing a better dispersion in water of the otherwise almost insoluble glyceride, and consequently, greatly improving its lubricity performance (as shown in the experimental results in Table I).

It is interesting to note that the pure XG is not able to significantly adsorb on the metal surface, as shown in Figure 5(c), in contrast with the XG : C12 complex behavior. It is thus suggested that, despite the fact that the complex formation allows for a better dispersion in water of the monoglyceride, it also decreases the solubility of the polysaccharide in water, which favors the adsorption on the metal surface, and therefore the performance as a lubricant.

As expected, the triester with a C10 hydrocarbon chain also showed a very low affinity for the iron surface, since its structure does not present any hydroxyl groups for its anchorage on

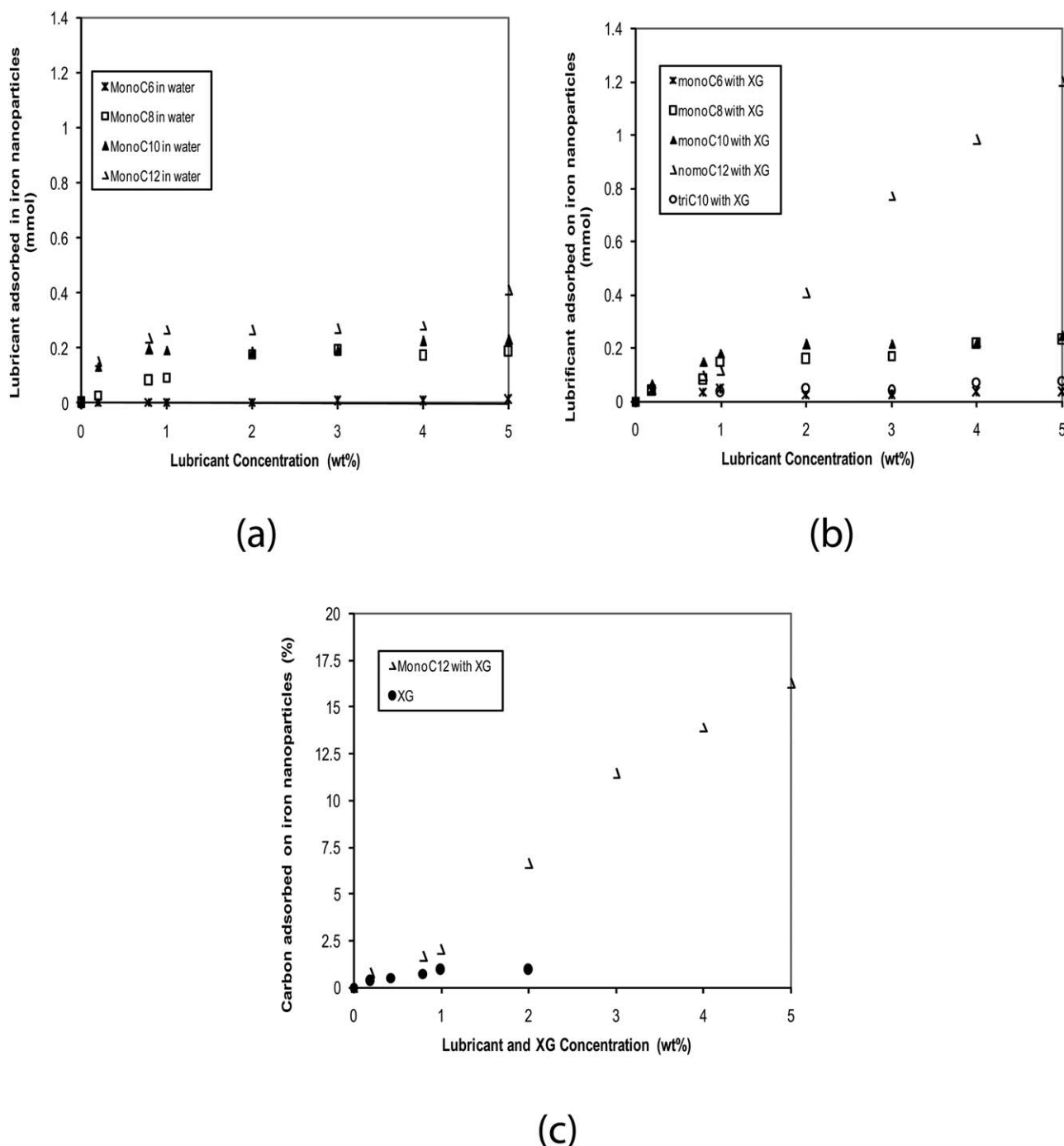


Figure 5. Adsorption curves of: (a) glycerides MonoC6, MonoC8, and MonoC10 in water, (b) glycerides MonoC6, MonoC8, MonoC10, and TriC10 with XG, (c) glycerides MonoC12 with XG.

it. The tests were performed only for the tridecanoate of glycerol, but all the triglycerides are expected to have a low affinity for the iron surface or for the XG due to the absence of free hydroxyl groups.

CONCLUSIONS

The results from the study of the aqueous mixtures of nonionic monoglyceride surfactants and XG showed that the interactions

occurring between these molecules are very important for their mechanism of action as lubricants in water-based drilling fluids. Experiments using tensiometry, contact angle, adsorption onto iron oxide nanoparticles, and lubricity tests produced evidence of the formation of a complex between those molecules that favored their adsorption on the metal surface. While monoglycerides with C8, C10, C12, and C18 carbon chains showed to be excellent lubricants in aqueous medium, with a steady improvement of their performance with the decrease of their

water solubility, the C6 derivative presented a much poorer performance, probably due to its much higher water solubility. Therefore, a monoglyceride to be used as a water-based lubricant under these conditions, should have a hydrocarbon chain longer than six carbon atoms, in order to stay adsorbed on the metal surface and ensure an appropriate lubricant film formation. Monoglycerides were able to reduce the FC even further when used in XG suspensions, suggesting that they are probably forming a complex with the polysaccharide that shows a synergy toward their performance as lubricants. The monooleate of glycerol (MonoC18 : 1) and monolaurate of glycerol (MonoC12) interacted better with XG, and exhibited excellent reduction of water FC compared to the others monoglycerides analyzed. The formation of the polysaccharide–surfactant complex improved their efficiency as lubricants because it helps to disperse the otherwise poorly soluble lubricants into water, allowing for further adsorption on the metal surface. The results obtained in this work also confirmed that the presence of one or more free OH groups in the polar segment of the molecular structure is very important for the lubricant to adsorb strongly on the metal surface or to interact with XG.

ACKNOWLEDGMENTS

The authors gratefully acknowledge CNPq and FAPERJ for the financial support.

REFERENCES

1. Li Ran, M.A.; Chen Hui, Z.; Shu Hai, L. *Chin. Sci. Bull.* **2012**, *57*, 2062.
2. Nagendramma, P.; Kaul, S. *Renew. Sustain. Energy Rev.* **2012**, *16*, 764.
3. Thomas, J.E. In *Fundamentos da Engenharia de Petróleo*; Rio de Janeiro **2001**, Chapter 4, p 80.
4. Spinelli, L. S.; Aquino, A. S.; Lucas, E.; d'Almeida, A. R.; Leal, R.; Martins, A. L. *Polym. Eng. Sci.* **2008**, *48*, 1885.
5. Peacock, D. W. US. Pat 3,215,628, November 2, **1965**.
6. Quigley, M. C.; Mobil R&D Corp. Advanced Technology for Laboratory Measurements of Drilling Fluid Friction Coefficient; Presented at the 64th Annual Technical Conference, Texas, **1969**, SPE paper 19537.
7. Knox, D.; Jiang, P.; Swaco, M-I. Drilling Further with Water-Based Fluids-Selecting the Right Lubricant; presented at the 2005 SPE international Symposium on Oilfield Chemistry, Texas, **2005**, SPE paper 92002.
8. Sonmez, A.; Kok, M. V.; Ozel, R. *J. Pet. Sci. Eng.* **2013**, *108*, 64.
9. Hirayama, T.; Torii, T.; Konishi, Y.; Maeda, M.; Matsuoka, T.; Inoue, K.; Hino, M.; Yamazaki, D.; Takeda, M. *Tribol. Int.* **2012**, *54*, 100.
10. Li, B. L.; Clarke, S. M.; Wilson, D. L. *Colloids Surf. A* **2011**, *389*, 180.
11. Velkavrh, I.; Kalin, M. *Tribol. Int.* **2012**, *50*, 7.
12. McNamee, C. E.; Yamamoto, S.; Kappi, M.; Butt, H.; Higashitani, K.; Dedinaite, A.; Claesson, P. M. *J. Colloid Interface Sci.* **2011**, *364*, 351.
13. Caenn, R.; Chillingar, G. V. *J. Pet. Sci. Eng.* **1996**, *14*, 221.
14. Hu, J.; Du, Z.; Li, C.; Min, E. *Fuel* **2005**, *84*, 1601.
15. Aoshima, H.; Miyagismma, A.; Nozawa, Y.; Sadzuka, Y.; Snob, T. *Int. J. Pharm.* **2005**, *293*, 25.
16. Boschkova, K.; Feiler, A.; Kronberg, B. *Langmuir* **2002**, *18*, 7930.
17. Yaakoub, M. C. Obtenção de ativos para fluido de perfuração a partir da glicerina. Msc. Thesis, UFRJ, April, **2008**.
18. Petri, D. F. S.; Queiroz Neto, J. C. *J. Pet. Sci. Eng.* **2010**, *70*, 89.
19. Khan, M. Y.; Samanta, A.; Ojha, K.; Mandai, A. *Asia-Pac. J. Chem. Eng.* **2008**, *3*, 579.
20. Pérez-Gramatges, A.; Matheus, C. R. V.; Lopes, G.; Da Silva, J. C.; Nascimento, R. S. V. *Colloids Surf. A* **2012**, *418*, 124.
21. Mukherjee, I.; Sarkar, D.; Moulik, S. P. *Langmuir* **2010**, *26*, 17906.
22. McNamee, C. E.; Yamamoto, S.; Kappi, M.; Butt, H.; Higashitani, K.; Dedinaite, A.; Claesson, P. M. *J. Colloid Interface Sci.* **2011**, *364*, 351.
23. Yu, C. C.; Lee, Y. C.; Cheon, B. S.; Lee, S. H. *Bull. Korean Chem. Soc.* **2003**, *24*, 8.
24. Silva, A. P. M.; Silva, J. F. C. *Org. Process Res. Dev.* **2011**, *15*, 893.
25. Silva, A. P. M.; Oliveira, P. B.; Bandini, T. B.; Barreto A. G. Jr.; Sena, R. C.; Silva, J. F. C. *Sens. Actuators B* **2013**, *177*, 1071.
26. Velkavrh, I.; Kalin, M. *Tribol. Int.* **2012**, *50*, 57.
27. Wu, Y.; Iglauer, S.; Shuler, P. J.; Tang, Y.; Goddard, W. A. *Tenside Surf. Det.* **2011**, *48*, 346.
28. Iglauer, S.; Wu, Y.; Shuler, P. J.; Tang, Y.; Goddard, W. A. Alkyl Polyglycoside Surfactants for Improved oil Recovery; Presented at the 2004 SPE/DOE 14th Symposium on Improved Oil Recovery, Oklahoma, **2004**, SPE paper 89472.
29. Bera, A.; Kumar, T.; Ojha, K.; Mandal, A. *Appl. Surf. Sci.* **2013**, *284*, 87.
30. Souza, C. E.; Lima, A. S.; Nascimento, R. S. V. *J. Appl. Polym. Sci.* **2010**, *117*, 857.
31. Kwon, C. W.; Yoon, T. S.; Yin, S. S.; Park, S. H.; Kim, K. B. *J. Nanopart. Res.* **2009**, *11*, 831.