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Effect of Surfactants on the Deformation and Detachment of Oil Droplets in a Model Laminar Flow Cell

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Résumé — Étude de l'effet de tensioactifs sur la déformation et le détachement de gouttes d'huiles modèles à l'aide d'une cellule à flux laminaire — Les tensioactifs « verts » à tête polaire dérivée de sucre (glucose, pentose) sont de plus en plus présents dans les formulations détergentes en raison des réglementations en vigueur et des demandes des consommateurs. Dans le but d'étudier le pouvoir détergent de ces nouvelles molécules, le comportement de gouttes d'huiles modèles soumises à un flux de solution détergente de concentration variable, a été étudié à l'aide d'une cellule à flux laminaire et corrélé aux propriétés physicochimiques des systèmes aux interfaces liquide/liquide et solide/liquide/liquide. Trois comportements principaux ont été observés à partir d'une valeur critique du débit de détergent : un étalement, un fractionnement de la goutte ou bien son détachement spontané de la surface. L'analyse des résultats a montré une corrélation entre le comportement de la goutte et l'équilibre des forces s'exerçant sur la goutte dans sa position initiale (avant l'application du flux), en particulier en considérant la force de gravité, qui tend à détacher la goutte de la surface, et la force capillaire, qui tend à maintenir sa forme sphérique. Un diagramme d'état a pu être établi, permettant de prédire le comportement de la goutte, en fonction du nombre de Bond (rapport des forces de gravité sur les forces capillaires) et du cosinus de l'angle de contact de la goutte dans sa position initiale. Les résultats obtenus ont permis de comparer les performances de différents tensioactifs en termes de dégraissage et d'illustrer le potentiel des AlkylPolyPentosides (APP) pour cette application.

Abstract — Effect of Surfactants on the Deformation and Detachment of Oil Droplets in a Model Laminar Flow Cell — Sugar-based surfactants are increasingly present in the development of eco-friendly detergents due to current regulations and consumer demand. In order to assess the degreasing performance of these new surfactants, the behavior of model oil droplets subjected to the action of a flow of surfactant solutions of different concentrations was studied in a laminar flow cell and related to the physico-chemical properties measured at the liquid/liquid (interfacial tension) and solid/liquid/liquid interfaces (contact angle). With the surfactant solutions and the model oils employed in this study, three main behaviors were observed when a critical flow rate was reached: elongation, fragmentation or spontaneous detachment of the droplet. The analysis of the results leads to a correlation between the droplet behavior and the balance of the forces applied on the droplet in

its initial position, in particular the gravity force F_g , which tends to move the oil droplet upwards (given the density difference), and the capillary force F_c , which tends to keep the droplet spherical. A state diagram could be established, based on the dimensionless Bond number (F_g/F_c) and $\cos \theta$, θ being the initial contact angle of the drop on the surface before the establishment of the flow. One can thus predict the droplet behavior as a function of the system initial characteristics. The results allowed the comparison of degreasing performance of the different surfactants used and illustrated the potential of AlkylPolyPentosides (APP) for detergent formulations.

INTRODUCTION

Detachment of liquid droplets from solid surfaces is of great importance in numerous fields of applications including enhanced oil recovery, degreasing, fabric detergency and membrane emulsification. In this paper, we focus on degreasing applications which consist in removing organic soils (oils, fats, waxes, inks, etc.) from a solid surface with a physical process.

The solvents most commonly used for this application are trichloroethylene, perchlorethylene and methylene chloride, as well as other classical solvents like methyl ethyl ketone, alcohols and aliphatic solvents. In 2007, the European market for degreasing solvents was reaching 152 000 tons [1]. The tonnage has continuously decreased since 2000, as new regulations have been set in place at the European level. These include the REACH (Registration, Evaluation, Authorization and restriction of CHemicals) regulation and other directives that aim at reducing emissions of VOC (Volatile Organic Compounds). They require new products to be formulated that will tend to be more environmentally friendly [2].

As a consequence, green solvents which operate, like classical solvents, by a solubilizing mechanism, have been promoted. Their performances can be predicted by various approaches [3, 4]. Another alternative consists in the development of aqueous detergent solutions based on agricultural renewable resources. In this study, we focus on AlkylPolyGlycosides (APG), green sugar-based surfactants, which are widely used in formulations [5], and on AlkylPolyPentosides (APP), which are more recent compounds. APP are considered as ethical surfactants, as they are obtained from local agricultural waste like wheat straw and bran. Our aim is to assess and compare their ability to degrease hard-surfaces. In this purpose, we will analyze the removal of model oil droplets from hard surfaces under the action of the flow of an aqueous surfactant solution.

The removal of soils from substrates by surfactants solutions is a complex problem, which depends on various parameters: the nature of the soil to be removed, the substrate or surface to which it clings, the process by which the soil is to be removed, the type of degreaser

to be used, its temperature, etc. [6]. Numerous studies have attempted to correlate oil removal with easily measurable physicochemical properties [7, 8]. Characterizing the degreasing performances as a function of the interfacial tension or contact angle at the three-phase system (hard-surface/oil/degreasing liquid) has provided a better understanding of several degreasing processes that are governed by physicochemical phenomena. Three main processes have been identified. Rolling-up occurs when the contact angle between the substrate, liquid soil and surfactant solution (described by Young's equation [9]) increases until the complete detachment of the oil droplet. During necking and emulsification, part of the oil is siphoned off into the degreasing liquid by hydrodynamic forces. In this case, the contact angle does not change appreciably but the interfacial tension between the oil and degreasing liquid decreases significantly until the oil partially detaches. The oil can otherwise be solubilized in the hydrophobic cores of surfactants micelles that adsorb on and then desorb from the solid surface.

A number of theoretical studies have considered the motion, deformation and detachment of pure droplets adhering to solid substrates under the effect of a pure liquid laminar flow, as detailed in reference [10]. In earlier models, the droplet was assumed to be a solid particle. Only complex numerical simulations modeling the continuous droplet deformation under flow have allowed good prediction of the drop behavior [10-12]. But these studies are restricted to simple fluid compositions and large contact angles (above 80°). A few experimental studies have investigated the problem [10, 12-15]. They have mainly aimed at characterizing the critical flow conditions above which droplets deform on the solid surface or detach from it in an irreversible manner. In the case of very high initial contact angles (~180°, decane or pristane / pure water / glass system), experimental results are in agreement with those predicted by the theory [11, 13]: the critical flow rate for droplet detachment correlates with physico-chemical parameters like the receding/advancing contact angles and interfacial tension, and also with the viscosity of the flowing fluid and droplet size. In the case of lower initial contact angles, experimental results show a more

complex picture than predictions and various droplet behaviors are observed when the flow rate is increased. Studies have evidenced various mechanisms, as sliding followed by detachment in the case of squalane / pure water / glass system (initial contact angle, 126° , oil-water interfacial tension, 51.7 mN/m) [13], slight elongation followed by detachment in the case of aniline / pure water / glass system (initial contact angle, 129° , oil-water interfacial tension, 5.27 mN/m) and elongation followed by fragmentation in the case of isoquinoline / pure water / glass system (initial contact angle, 84° , oil-water interfacial tension, 0.6 mN/m) [12].

The presence of surfactant considerably affects the droplet behavior under laminar flow: Dodecyl Trimethylammonium Bromide (DTAB) added to pristane (25 mg/L), in a pristane / pure water / glass system, results in an increased critical flow rate for droplet detachment, while the contact angle and interfacial tension are not noticeably affected [15]. The presence of a commercial detergent (1.2% v/v, in water) in a system consisting in sunflower oil / pure water / stainless steel (initial contact angles, 134.6° and 144.9° , oil-water interfacial tension, 9.4 and 15.8 mN/m , with or without detergent respectively) has been also studied by Thoreau *et al.* [14]. In the absence of detergent, the oil droplet elongates and then fragments (a small residual quantity of oil remaining attached to the solid), while it slides without residual oil on the solid in case of the presence of detergent in water. Adding surfactant to pure water also has the effect to significantly reduce the critical flow rate for droplet detachment.

In order to find a generality in the results, theoretical and experimental studies have expressed their findings as a function of dimensionless numbers [10, 12, 13]. The dimensionless numbers that play a role in degreasing are the capillary number Ca , which is the ratio of viscous to interfacial forces, the Reynolds number Re , which is the ratio of inertial to viscous forces and the Bond number Bo , which is the ratio of gravitational to capillary forces. The capillary and Reynolds numbers account for the dynamic effects of the shearing fluid flow on the droplet. The Bond number characterizes the natural propensity of the droplet to deform because of buoyancy effects: it is only a function of the physicochemical properties of the fluid. Critical Ca and Re can be easily deduced from critical flow rate values. Several computational fluid dynamics simulations showed that critical Ca and Re are not only a function of the contact angle hysteresis but also of the initial size of the droplet [10, 12]. Seevaratnam *et al.* [10] combined Ca and Re in a new dimensionless number G defined as Ca^2/Re . From their experimental results, they constructed “flow maps” (Ca versus G) that delineate the critical conditions between droplet sliding, crawling or detachment.

In the present work, the degreasing performance of eco-friendly sugar based surfactants is assessed using an experimental set-up similar to the one developed by Thoreau *et al.* [14]. Single oil droplets initially deposited on a hard surface placed in a rectangular shear flow cell are subjected to a pressure-driven flow of surfactant solution. The deformation and/or detachment of the droplet are recorded through a vertical quartz window with a CCD camera. The surfactant concentrations are varied as well as the nature of the oil. Our objective is to evaluate the ability of APG and APP surfactants to remove various oils from the hard surface and to develop predictive behavior-maps based on the analysis of the physicochemical parameters of the three-phase system (hard-surface/oil/surfactant solution). Experimental conditions are chosen in order to be close to real industrial cleaning conditions: surfactant solutions are used at basic pH and 40°C , and soil is modeled by complex industrial oils.

1 MATERIALS AND METHODS

1.1 Materials

Three industrial grade surfactants with C8/C10 hydrocarbon chain length are studied: Appyclean 6781 (*Wheatoleo*, France) referred to as “APP” even though it is a blend of 70% APG and 30% APP (APP are synthesized by a Fischer’s glycosylation between pentoses (xylose and arabinose), issued from the hydrolysis of hemicellulose, and fatty alcohols obtained from vegetable oils [16]), Glucopon 215 UP (*Cognis*, France) and Simulsol SL8 (*SEPPIC*, France), which are 100% APG, denoted APGlu1 and APGlu2 respectively. Degreasing solutions are prepared with ultrapure water with six concentrations in surfactant: 0, 0.2, 0.4, 0.6, 0.8 and 1 g/L . The pH is adjusted to 10 (with NaOH, 0.1 M) before the introduction of the surfactant. The critical micelle concentrations are 0.45, 0.6 and 0.96 g/L for APP, APGlu1 and APGlu2 respectively (measured with the Wilhelmy plate method at 25°C in ultrapure water). The aqueous surfactant solutions are used at a temperature of 40°C . Density and viscosity of all degreasing solutions are similar to those of pure water in the same conditions (40°C) (*Tab. 1*). Four oils are used as model soil: a vegetable oil, Olive oil O1514 (*Sigma*), two industrial oils, Castrol® Variocut C215, Castrol® Rustilo 4169 (*BP*, Cergy-Pontoise, France) and an alkane, hexadecane (*Sigma*). Density and viscosity of oils are summarized in *Table 1*. Interfacial tension between oils and aqueous surfactant solutions is determined by the pendant drop technique with a Krüss

TABLE 1
Physical properties of degreasing solutions and oils (at 40°C)

	Density (kg.m ⁻³)	Viscosity (mPa.s)
Surfactants solutions (water, 40°)	992	0.65
Olive oil	900	19.64
Castrol® Variocut C215	860	13.97
Castrol® Rustilo 4169	860	8.62
Hexadecane	769	2.98

DSA 10 (*Krüß*, Hamburg, Germany). To determine interfacial values which are less than 2 mN/m, the spinning drop method, with a SITE04 (*Krüß*, Hamburg, Germany) tensiometer, was employed. The results are provided in Table 2. The measurement accuracy is ± 0.5 mN/m for the pendant drop method and ± 0.02 mN/m for the spinning drop method. The geometric characteristics of the droplet (contact angle, droplet height and contact diameter, droplet volume) are measured with the Krüss DSA 10 image analysis system. The accuracy of the contact angle measurement is $\pm 0.5^\circ$. All the physicochemical parameters are measured at 40°C.

The model hard surface consists in stainless-steel AISI310 (*GoodFellow*, England). Its dimensions are 2 mm \times 20 mm \times 33 mm. It is systematically subjected to the following stringent cleaning protocol before each experiment: cleaned with acetone (*Technical*, VWR), rinsed with ultrapure water and dried at 60°C for 5 min.

The surfactant degreasing performances are evaluated using a device made of a laminar flow-cell combined with Krüss DSA 10 as the frame acquisition system. The cell is a rectangular channel (5 mm \times 30 mm \times 230 mm) with a glass window on each lateral side, through which the behavior of oil droplet under flow can be observed [14]. The aqueous surfactant solution, maintained at 40°C in a water bath, is driven into the channel by a peristaltic pump (*Watson Marlow* SCIQ323).

1.2 Method

After fixing the hard-surface sample into the cell and filling the cell with the surfactant solution, an oil droplet (1-2 μ L) is deposited on the immersed hard surface with a 1 mL syringe through a 0.5 mm diameter needle. About 1 minute is needed for the droplet to reach its equilibrium shape. The initial contact angle and droplet

geometry are measured on the droplet at equilibrium (*Fig. 1*). In all the experiments, the droplet is about 1 mm high and has a contact diameter of 1.5-2 mm with the hard surface. The surfactant solution is then set in flow, the flow rate being slowly increased by steps of 0.7 mL/s until the drop deforms. Above a critical flow velocity U_c , the deformation of the drop is irreversible, meaning that the original form of the drop is not recovered when the flow is stopped. The flow velocity is defined by the flow rate delivered by the pump divided by the cell cross-section at the level of the droplet (110 mm²). Images of the droplet shape are continuously taken by the CCD Camera of the Krüss DSA 10 and recorded from the moment the aqueous solution flow is set until the droplet is irreversibly deformed. Three to five independent runs are performed for each fluid couple in order to check the reproducibility.

2 RESULTS AND DISCUSSIONS

2.1 Behavior of Oil Droplets Submitted to a Flow of Degreasing Solution

At low flow rates, the droplet experiences a slight oscillation under the influence of the flow, but it recovers its initial shape and dimension when the flow is stopped. Above a critical value of the flow rate (corresponding to U_c), an irreversible deformation of the droplet is observed. With the surfactant solutions and the model oils employed in this study, three main behaviors can be observed above the critical flow rate: elongation, fragmentation or spontaneous detachment of the droplet:

- elongation of the droplet (*Fig. 2a*): the droplet starts to move and spreads along the hard surface in the direction of the flow, leaving a mark of oil behind;
- partial fragmentation (*Fig. 2b*): stretching and necking of the droplet are observed, followed by a partial fragmentation of the droplet. A droplet residue remains on the surface and the same phenomenon can be observed repeatedly when the flow rate is further increased;
- spontaneous fragmentation (*Fig. 2c*): the phenomenon observed is similar to the previous one but it occurs spontaneously, without any external liquid flow. In this case, the detachment of the droplet from the surface starts as soon as the droplet is deposited on the surface. A residue remains on the surface and fragmentation can be observed successively several times.

In some cases, an intermediate behavior, that combines the two first ones, was observed. First, the oil droplet spreads on the surface, and then the edge of the droplet is stretched and fragmented.

TABLE 2

APP surfactant solution/oil systems in the laminar flow cell (40°C, pH 10): system behavior as a function of the initial physicochemical properties

c (g/L)	γ (mN/m)	θ (°)	Droplet behavior	U_c (m/s)
Olive oil				
0	25.5	90.4	Elongation	0.31
0.2	12.2	107.9	Elongation	0.21
0.4	7.1	119.9	Fragmentation	0.08
0.6	4.7	123.9	Fragmentation	0.04
0.8	2.7	107.9	Fragmentation	0.02
1	1.0	115	Fragmentation	0.02
Variocut®				
0	7.8	80	Elongation	0.25
0.2	4.3	76.4	Elongation	0.17
0.4	2.8	74	Elongation + fragmentation	0.10
0.6	1.4	84.5	Fragmentation	0.02
0.8	0.08		Spontaneous fragmentation	0
Rustilo®				
0	2.8	67	Elongation	0.16
0.2	2.3	68.5	Elongation	0.10
0.4	2.0	66.2	Elongation + fragmentation	0.08
0.6	1.8	66.7	Elongation + fragmentation	0.05
0.8	1.6	62.5	Elongation + fragmentation	0.05
1	1.4	61.8	Elongation + fragmentation	0.04

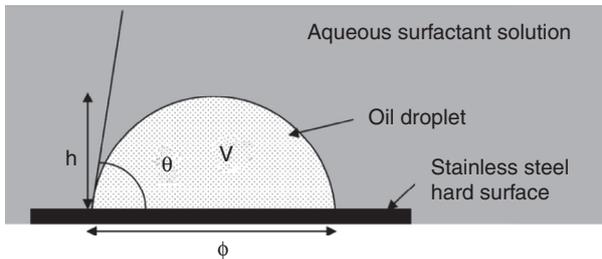


Figure 1

Schematic diagram of a droplet of volume V , when in equilibrium on the hard surface in the quiescent aqueous surfactant solution (initial condition). θ is the equilibrium contact angle, h the equilibrium droplet height and ϕ the equilibrium contact diameter.

2.2 Relating Drop Behavior and Interfacial Properties

For each oil and surfactant solution studied, the physicochemical parameters in the initial conditions (contact angle, interfacial tension) and the geometrical parameters of the droplets are determined and related to the behavior of the droplet under the external flow. The typical results obtained for the APP surfactant are gathered in Table 2.

Table 2 shows that, at low surfactant concentrations, when the interfacial tension is the highest, elongation and spreading of the oil droplet on the surface are observed at the highest values of the flow critical velocity. When the surfactant concentration increases, the

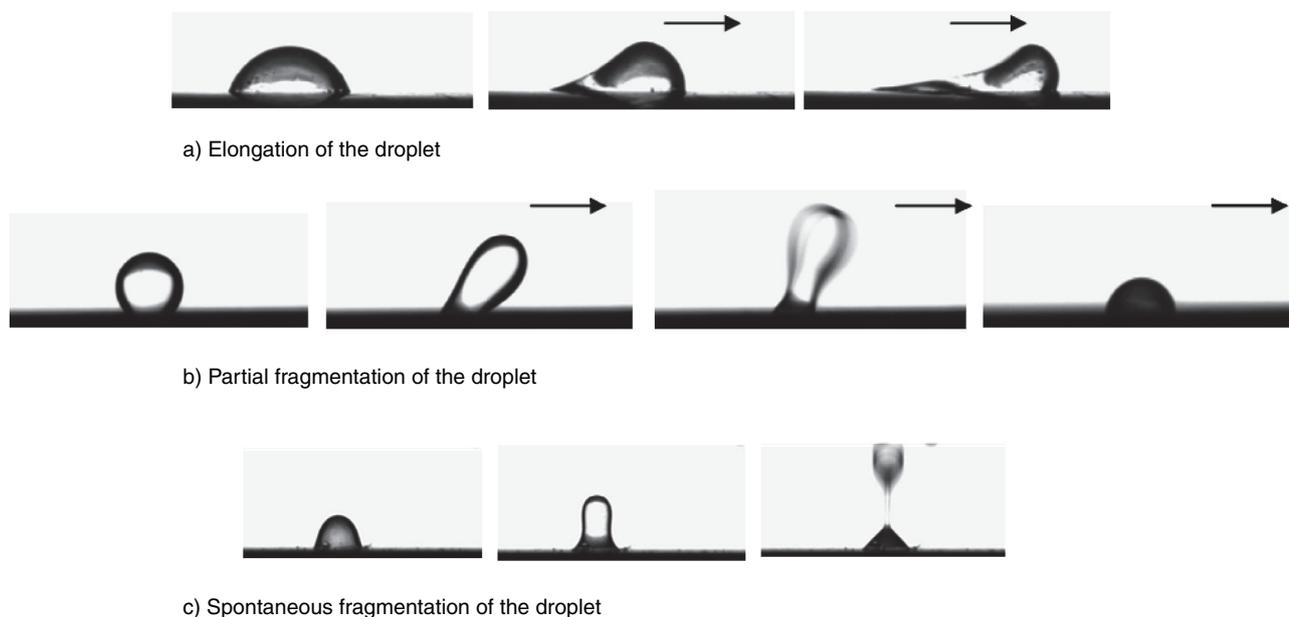


Figure 2

Possible behaviors observed when an oil droplet is deformed under the effect of a laminar flow (for flow velocities above the critical velocity U_c).

interfacial tension decreases, and a fragmentation of the droplet is then observed for lower values of the critical velocity. When the interfacial tension is high, the critical flow velocity is large, as the droplet resists flow deformation. The hydrodynamic force is then responsible for the irreversible deformation of the droplet. When the interfacial tension is low, droplets are easily deformable and more sensitive to the action of the flow: they stretch and fragment already at low flow velocities. If the interfacial tensions are very low, the fragmentation occurs spontaneously, *i.e.* without the action of the flow.

The same tendency is observed for the different oils employed but at different values of the interfacial tension, which cannot alone explain the phenomena observed. Other factors, such as the droplet size and the initial contact angle, are important parameters. For example, low contact angles promote the spreading of the droplet, whereas high contact angles (mainly above 90°) favor the fragmentation of the droplet.

2.3 Predictive State Diagram

In order to predict the behavior of an oil droplet under the flow of a surfactant degreasing solution, a state diagram has been drawn with all the results obtained, based on the ratio of the vertical forces applied on the oil droplet in the initial conditions.

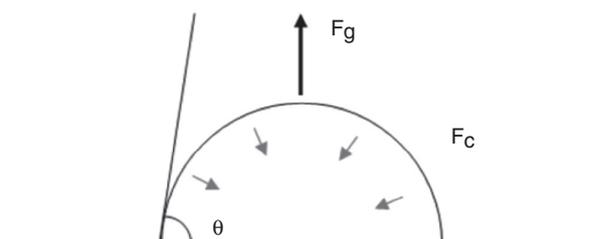


Figure 3

Schematic representation of the vertical forces applied on the oil droplet in its initial conditions.

The two main forces that act on the drop are the gravitational and capillary forces, as shown schematically in Figure 3. The buoyancy force F_g tends to detach the droplet from the hard surface, the oil having a lower density than the surfactant solutions.

It can be expressed as:

$$F_g = (\rho_{water} - \rho_{oil}) \times g \times V \quad (1)$$

where ρ_{water} and ρ_{oil} are the density of the aqueous phase and of the oil, g is the gravitational acceleration and V is the droplet volume. The capillary force F_c tends to compete against any deformation of the droplet:

$$F_c = \gamma \times \ell \quad (2)$$

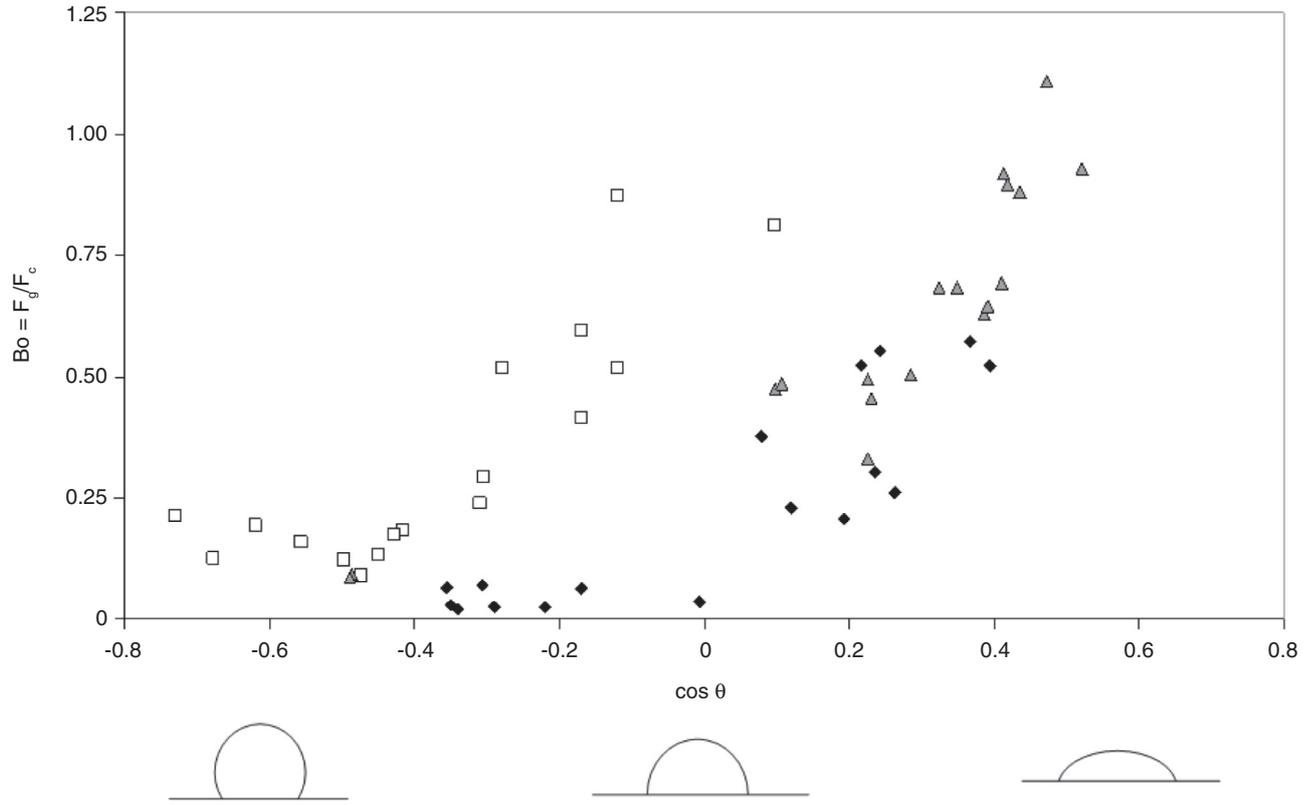


Figure 4

Droplet behavior at the critical flow velocity as a function of the Bond number Bo and cosine of the contact angle (elongation (black diamonds); fragmentation (white squares); elongation followed by fragmentation (grey triangles)).

where γ is the interfacial tension. The droplet contour length ℓ can be related to the droplet height h and contact diameter ϕ by:

$$\ell = 2\theta \times r \quad (3)$$

where θ is the contact angle in rad and r the radius of the sphere in which the droplet is inscribed:

$$r = \frac{h^2 + \left(\frac{\phi}{2}\right)^2}{2h} \quad (4)$$

We will define the ratio of the gravitational force to the capillary force F_g/F_c using equations (1-4) and denote it Bo for Bond number, as defined in the introduction.

On the state diagram in Figure 4, we have indicated the drop behavior for the various oils and surfactant solutions used, once the critical flow velocity is reached.

It is shown as a function of the values of the Bond number Bo and cosine of the contact angle.

Negative values of $\cos \theta$ (left-hand side of the diagram) correspond to high contact angles ($\theta > 90^\circ$), and positive values, to low contact angles ($0^\circ < \theta < 90^\circ$). Large values of the Bond number (top of the diagram) are obtained when the buoyancy force dominates surface tension effects: it corresponds to a large difference in density of the two phases, as all the droplets have a similar volume or a low interfacial tension. On the contrary, low values of the Bond number (bottom of the diagram), reflect a dominant capillary force over buoyancy effects.

As shown in Figure 4, each type of behavior observed at the critical flow velocity tends to gather in a particular region of the diagram. When the initial contact angle is high enough (left-hand side of the diagram), a low Bo number is sufficient to stretch and fragment the droplet, even in the case of rather high interfacial tension or

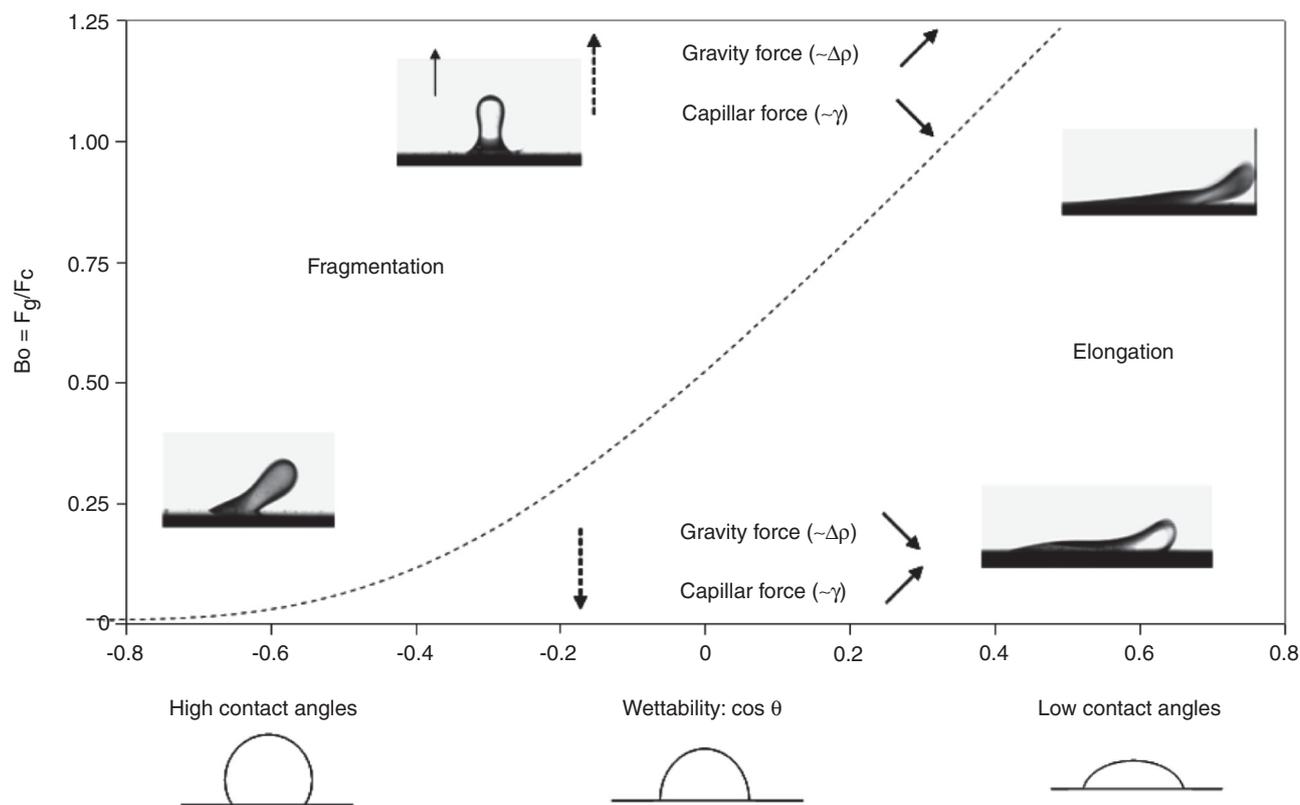


Figure 5

Diagram predicting the behavior of the oil droplet when the critical flow rate is reached.

low density difference. As the contact angle progressively decreases, a higher Bond number is required to observe a fragmentation of the droplet: it thus requires a higher density difference or a lower interfacial tension. When the contact angle is very low, we typically observe the elongation of the droplet.

By taking into account all these observations, one can draw the schematic state diagram shown in Figure 5. It divides the space into two main regions, droplet fragmentation taking place on one side, elongation on the other. The two regions are delimited by the dotted curve in Figure 4.

In the region of high contact angles, the droplet is easily fragmented. On the bottom left-hand side of the diagram, the fragmentation is induced by the flow but it can be spontaneous, when the interfacial tension is very low (top left-hand side). At low contact angles and Bond numbers (bottom right-hand side), the droplet remains very close to the surface and spreads along it with the flow. At higher

Bo number, the spreading phenomenon can be followed by a partial fragmentation of the edge of the droplet.

Such a diagram helps to find and predict the appropriate conditions in which fragmentation and/or elongation occurs. It can be applied either to remove an oil droplet from a surface as in degreasing applications, or to spread a protective coating (*e.g.* a biocide) on a surface, which could be difficult to reach.

2.4 Application: Comparison of the Degreasing Performance of the Agrosurfactants

To compare the degreasing performance of different surfactants, one can compare the critical flow velocity necessary to observe the fragmentation of the droplet. In the example shown in Figure 6, a lower critical rate is required with the surfactant blend containing alkylpolyentose molecules to observe the fragmentation of an olive oil droplet compared to the results obtained

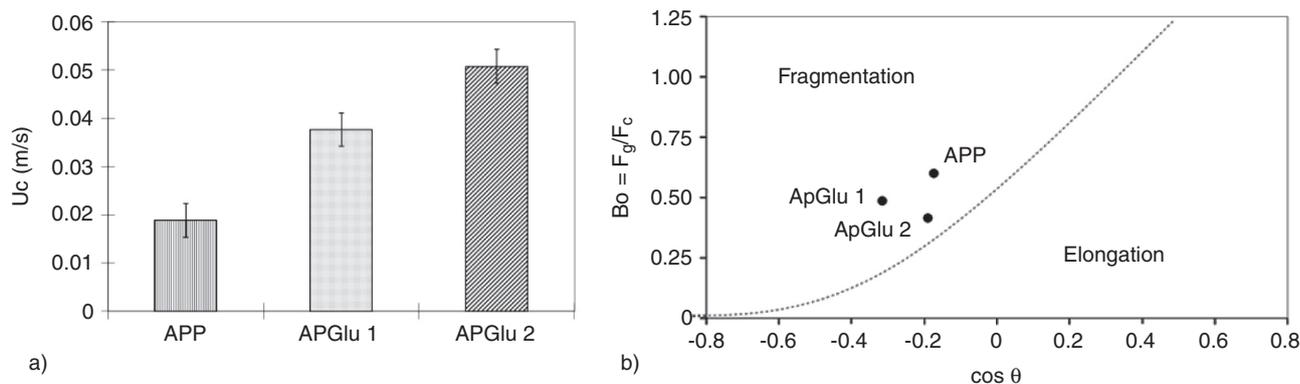


Figure 6

Comparison of the degreasing performance of the three agrosurfactants at a concentration of 1 g/L, in presence of an olive oil droplet: a) comparison of the corresponding critical flow velocities; b) position of the three surfactants in the state diagram.

with alkylpolyglucoside surfactants at a concentration of 1 g/L (at 40°C and pH 10). Their relative position in the state diagram (Fig. 6b) reflects a lower interfacial tension with APP, due to a smaller polar head more lipophilic, promoting a lower critical flow velocity for droplet fragmentation.

CONCLUSION

The development of new green agrosurfactants detergent formulations is a valuable alternative to petrochemical solvents, in particular for degreasing applications. The behavior of model industrial oil droplets deposited on a hard surface was studied in experimental conditions close to industrial applications (circulation of surfactant solutions at 40°C, pH 10). This study allowed the build-up of a predictive state diagram, in which the two main phenomena observed, fragmentation and elongation of the oil droplet, were shown to depend on the initial interfacial characteristics of the droplet and flow conditions. The degreasing power of different surfactants can be assessed by comparing the critical flow velocity required for the fragmentation of the droplet.

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REFERENCES

- De Caro P., Thiebaud-Roux S. (2008) Biosolvants, *Techniques de l'Ingénieur* **IN 102**, 1-9.
- Lemor A. (2006) Directives COV et alternative lipochimique: peintures, encres, nettoyage, dégraissage, *Oléagineux, Corps Gras Lipides* **13**, 2-3, 171-177.
- Fréville V., van Hecke E., Marinkovic S., Ernenwein C., Pezron I. (2011) Mapping and multivariate analysis for a rapid evaluation of new green solvents characteristics and efficiency, *J. Dispers. Sci. Technol.* **32**, 1742-1752.
- Moity L., Durand M., Benazzouz A., Pierlot C., Molinier V., Aubry J.-M. (2012) Panorama of sustainable solvents using the COSMO-RS approach, *Green Chem.* **14**, 4, 1132-1145.
- Ware A.M., Waghmare J.T., Momin S.A. (2007) Alkylpolyglucoside: carbohydrate based surfactant, *J. Dispers. Sci. Technol.* **28**, 437-444.
- Wery M. (1998) Dégraissage, *Techniques de l'Ingénieur* **M 1 450**, 1-26.
- Verma S., Kumar V.V. (1998) Relationship between oil-water interfacial tension and oily soil removal in mixed surfactant systems, *J. Colloid Interface Sci.* **207**, 1-10.
- Miller C.A., Raney K.H. (1993) Solubilization-emulsification mechanisms of detergency, *Colloids Surf. A: Physicochem. Eng. Aspects* **74**, 169-215.
- Young T. (1805) An essay on the cohesion of fluids, *Philos. Trans. R. Soc. Lond.* **95**.
- Seevaratnam G.K., Ding H., Michel O., Heng J.Y.Y., Matar O.K. (2010) Laminar flow deformation of a droplet adhering to a wall in a channel, *Chem. Eng. Sci.* **65**, 4523-4534.
- Basu S., Nandakumar K., Masliyah J.H. (1997) A model for detachment of a partially wetting drop from a solid surface by shear flow, *J. Colloid Interface Sci.* **190**, 253-257.
- Gupta A.K., Basu S. (2008) Deformation of an oil droplet on a solid substrate in simple shear flow, *Chem. Eng. Sci.* **63**, 5496-5502.

- 13 Mahé M., Vignes-Adler M., Rousseau A., Jacquin C.G., Adler P.M. (1988) Adhesion of droplets on a solid wall and detachment by a shear flow. I. Pure systems, *J. Colloid Interface Sci.* **126**, 314-328.
- 14 Thoreau V., Malki B., Berthome G., Boulangé-Petermann L., Joud J.C. (2006) Physico-chemical and dynamic study of oil-drop removal from bare and coated stainless-steel surfaces, *J. Adhesion Sci. Technol.* **20**, 16, 1819-1831.
- 15 Mahé M., Vignes-Adler M., Rousseau A., Jacquin C.G., Adler P.M. (1988) Adhesion of droplets on a solid wall and detachment by a shear flow. III. Contaminated systems, *J. Colloid Interface Sci.* **126**, 337-345.
- 16 Martel F., Estrine B., Plantier-Royon R., Hoffmann N., Portella C. (2010) Development of agriculture left-overs: fine organic chemicals from wheat hemicellulose-derived pentoses, *Top Cur. Chem.* **294**, 79-115.

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