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INFLUENCE OF LIQUID SURFACE TENSION (SURFACTANTS) ON BUBBLE FORMATION AT RIGID AND FLEXIBLE ORIFICES

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Abstract.

The influence of liquid surface tension on the bubble formation from both rigid and flexible orifice has been investigated. The liquid phases under test are aqueous solutions with butanol or surfactants (cationic, non-ionic and anionic); static and dynamic measurements of liquid surface tension have been performed to characterise them. This study shows that the effect of surface tension on the bubbles generated cannot be analysed only in terms of the static surface tension, but also depends on whether the bubbles are generated from a rigid orifice or from a flexible orifice. The kinetics of adsorption and diffusion of the solute molecules towards the bubble interface have to be taken into account insofar as their time scales are comparable to those of the bubble formation phenomenon.

1. Introduction

A variety of chemical engineering processes are based on the use of gas-liquid reactors. The gas is released in the form of small bubbles to yield a large surface area and also an efficient mass transfer between gas and liquid phases. Depending on the process, various gas spargers are used as aeration systems:

- in chemical industries, the aeration of the liquids is mainly performed with rigid nozzles (perforated plate, porous disk diffuser) as they are able to withstand high temperatures and pressures;

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- for waste water treatment, carried out under atmospheric conditions, a gas sparger based on flexible membranes has been developed. This punctured rubber sheet has been reported to produce very uniform size distribution of small bubbles which leads to large increases in gas hold-up and mass transfer area [1]. Moreover, it is found to be self-cleaning and does not suffer the usual clogging problems when aeration is stopped in the tank (anaerobic period).

The gas sparger plays a crucial role insofar as it has a direct influence on the hydrodynamics of the liquid and gaseous phases and therefore on the mass transfer [2-3]. Indeed, the bubble size in the reactor is the result of the bubble formation step and of the coalescence and breakage bubble processes in the liquid medium. The present study focuses on the initial step, namely on the bubble generation at the gas sparger orifice.

With regard to its importance and to its complexity, the bubble formation phenomenon has been the subject of many experimental and theoretical studies: two detailed reviews of the literature are given by [4-5]. However, a surprising lack of research concerning the bubble formation at a flexible orifice has been observed : only a limited number of works can be noted [6-13].

In chemical industries or for waste water treatment, the liquid phases commonly found are very complex due to the presence of several compounds and to the operating conditions (high temperature and pressure). Consequently, a lot of research has been performed to understand the influence of the liquid phase properties on the bubble formation phenomenon. Nevertheless, whilst the liquid density and viscosity have been widely studied, the liquid surface tension and its effects are largely an unknown factor. In the works where the liquid surface tension is considered, its influence is not really separated from those of liquid density and viscosity [14-15] and they are limited to the use of organic liquids. In particular, the effect of surfactants on the bubble formation phenomena remain a scientific area virtually

unexplored in spite of its practical and industrial value [16-17].

To fill the gap, the general aim of this paper is to study the influence of liquid surface tension on the bubble formation phenomenon. The originality of this work is two-fold:

- the use of surfactants and butanol aqueous solutions as liquid phases (the solutions being dilute, the effects of liquid viscosity and density are excluded),
- the comparison of their effects on the bubble formation as a function of the gas sparger nature, i.e rigid and flexible orifices.

To this effect, this paper will be composed of three sections. First, the material and the experimental methods used will be described. Secondly, the characterisation of the liquid phases under test will be presented in terms of static and dynamic measurements of liquid surface tension. The last section will be devoted to the study of the impact of surface tension on the dynamics of bubble growth and detachment, on the nature of the bubbles generated from a rigid orifice and from a flexible orifice respectively.

2. Material and methods

2.1 *Material*

a) Experimental set-up

The experiments are carried out in a temperature controlled (20 °C), glass parallelepiped vessel, 0.40 m in width, 0.40 m in length and 0.50 m in height (Figure 1). The gas flow rate is regulated by a pressure gauge and by a gas flow meter. The pressure drop created by the sparger is determined using an electronic Bioblock 915PM247 type manometer. The average gas flow rate Q_G is measured using a soap film meter, through a funnel (1.5 cm diameter) put on the orifice. Air is used as gaseous phase.

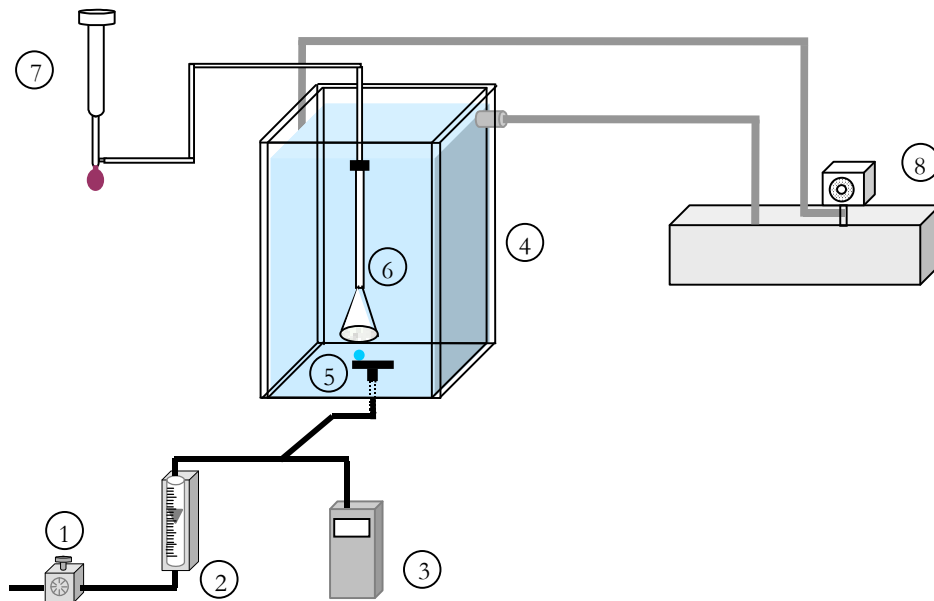


Figure 1 Diagram of the experimental set-up

[1. Pressure gauge, 2. Gas flow meter, 3. Electronic manometer, 4. Glass vessel, 5. Gas sparger orifice, 6. Funnel, 7. Soap film meter, 8. Temperature control]

b) Gas spargers

The experimental set-up previously described can be equipped with a flexible membrane or with a rigid orifice as gas sparger:

- Rigid orifice. One stainless steel tube is used as the rigid sparger with 12 mm external diameter and 8 mm internal diameter. The tube is perforated in order to obtain an orifice of 0.7 mm in diameter (Figure 2.a).
- Flexible orifice. An industrial rubber membrane sparger (called M1) is used as flexible sparger. The bubbles are generated by a single puncture located at the membrane centre. The membrane (60 mm diameter) is assembled on a circular clamping ring composed of two jaws (Figure 2.b); this fixing system coupled with the use of a dynamometric spanner enables the same initial tension to be applied, thus giving reproducible results.

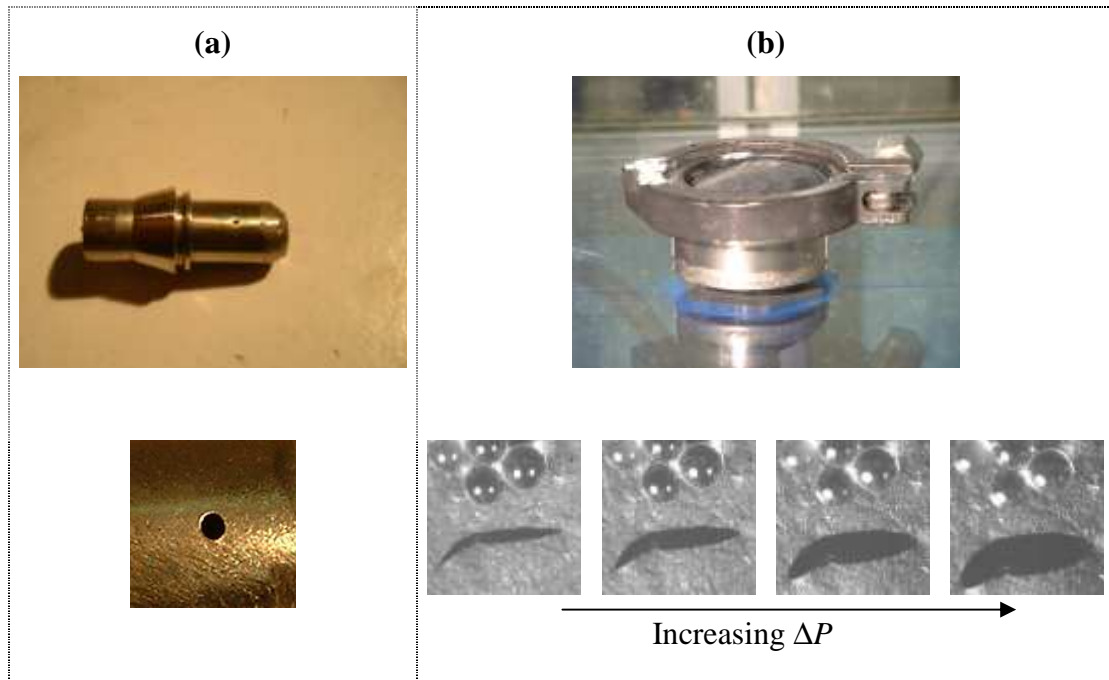


Figure 2. Gas spargers

(a) Rigid orifice. (b) Flexible membrane: fixing system and expanding orifice photographs.

The physical characteristics of both orifices and the operating conditions are shown in Table 1. Note that the gas flow rates studied correspond to the static and dynamic bubbling regimes, the jetting regime is not considered. In addition, it is important to bear in mind that the particular nature of these orifices is fundamentally different. Whilst the rigid orifice is not distorted whatever the gas flow rate, the flexible orifice is punctured in a stretched rubber sheet, so its important feature is its elastic nature [12]. To have a complete characterisation of both orifices in terms of physical properties, the authors advice consulting [11].

Table 1. Physical characteristics of both orifices and operating conditions. ⁽¹⁾ The membrane bulging is not included. ⁽²⁾ Measured under a liquid height H_L . ⁽³⁾ Measured by using a camera coupled with a microscope, the equivalent orifice diameters used correspond to the diameter of circular hole with the same area [12]

Parameters	Thickness (mm)	$V_C^{(1)}$ (cm ³)	γ_C (mN/m)	$\Delta P_C^{(2)}$ (mbars)	H_L (m)	$d_{OR}^{(3)}$ (mm)	Q_G (ml/s)	U_{OR} (m/s)
Rigid Orifice	2.00	33.4	19	32	0.33	0.7	0.16 - 3.21	0.42 - 8.35
Flexible Orifice	2.15	101	23	115	0.20	0.35 - 0.45	0.10 - 2.34	0.98 - 14.59

c) *Liquid phases*

The experiments are performed using different liquid phases: tap water, an aqueous solution of butanol and several aqueous solutions of surfactants. The surfactants have been chosen with regard to their nature and to their application (waste water treatment). Three types of surfactants are considered:

- An anionic surfactant (sodium laurylsulfate; $M \approx 382$ g/mol),
- A non-ionic surfactant (fatty alcohol C 12/18-10 EO, n-butyl end-capped; $M \approx 700$ g/mol),
- A cationic surfactant (lauryl dimethyl benzyl ammonium bromine, $M \approx 400$ g/mol).

Whatever their nature, the molar concentration of surfactants is taken equal as $3.75 \cdot 10^{-3}$ mol/l in order to be representative of those found in waste waters. The required quantity of surfactants is weighed, dissolved in a volume of water and homogeneously introduced into the vessel, taking care not to form any foam.

The aqueous solution of butanol is obtained from a mother solution (810 kg/m³, purity of 99.8%) with 0.5% in volume, i.e. $5.5 \cdot 10^{-2}$ mol/l.

2.2 *Methods*

a) *Image acquisition and treatment systems*

During their formation, bubbles are photographed with a Leutron LV95 camera (360 images/s). Images are visualised on the acquisition computer through the Leutron vision software. The Visilog 5.4 software performs the image treatment. The following parameters are determined: equivalent bubble diameter ($d_B \pm 12\%$), centre of gravity co-ordinates (x,y), eccentricity (χ), contact angle ($\theta \pm 15^\circ$) and surface/bubble contact diameter ($d_w \pm 15\%$). The bubble formation time is deduced from photographic analysis ($T_B \pm 2.78$ ms).

b) *Surface tension measurements*

Static method. These measurements are performed by the Prolabo tensiometer based on the Wilhelmy plate method and by the Krüss tensiometer based on the pendant drop method. The special nature of these methods leads to a major drawback: the surface age is not taken into account.

Dynamic method. During the bubble growth, the contact time between gas and liquid is several seconds; thus, the adsorption and diffusion kinetics of solute molecules towards the interface must not be neglected and can have consequences on the bubble size and the associated growth time. For these reasons, the use of a dynamic surface tension method becomes essential insofar as it offers the possibility to determine surface tension for different bubble surface ages. The technique used is the bubble pressure one [18]. The apparatus (Figure 3) is divided into three parts: (1) the measurement cell containing the solution under test in which a capillary is submerged, (2) the pressure sensor that gives the detachment pressure of the bubble (liquid height difference), and (3) the apparatus to create the pressure necessary to liberate the bubble from the capillary.

The measurement is based on the continuous measurement of the applied pressure versus bubble rate formed at the tip of the capillary. A high bubble formation rate is equivalent to a short surface age. With this technique, surface ages between about 2 ms and 60 s can be

achieved. Using the geometric characteristics of the apparatus, it is possible to deduce the surface tension of the solution for a given bubble formation time [18,11].

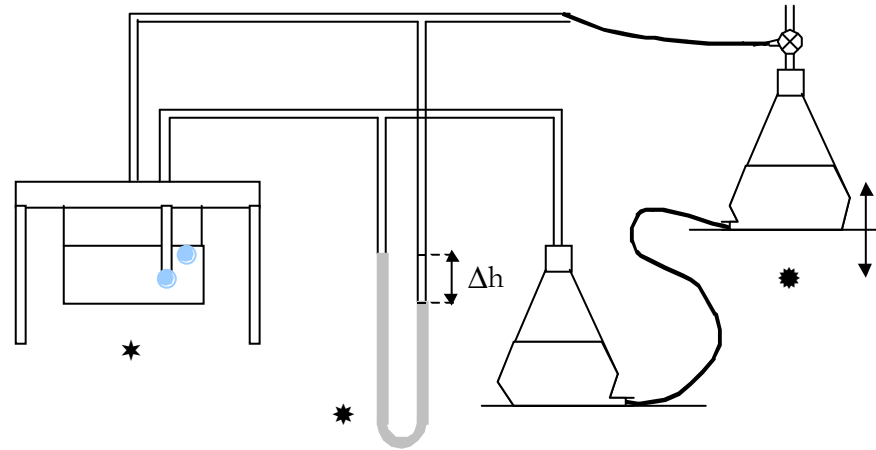


Figure 3. Diagram of the surface tension dynamic method

3. Liquid phase characterisation

To understand the effects of liquid surface tension on the bubble formation, it is first essential to accurately characterise the liquid phases under test: this is the aim of this part.

Note that, as our liquid phases are dilute aqueous solutions, their density and their viscosity can be approximated to those of tap water. The liquid phase characterisation is then restricted to the determination of their surface tension and the associated properties.

3.1 Properties related to static surface tension measurements

The principle of the static methods is based on the measurement of the surface tension when the adsorption equilibrium is reached, i.e. for infinite surface ages.

In this section, the properties related to the static surface tension measurements will be presented: the static surface tension value of the different liquid phases, the Critical Micellar

Concentration (CMC) of the surfactant aqueous solutions and their characteristic adsorption parameters (Γ_∞ , K , ΔG_0 , s_e).

a) *Static surface tension*

The static surface tension of the liquids under test is reported in Table 2. The lowest surface tension is obtained for the cationic surfactant solution and the highest for the butanol solution.

Table 2. Liquid phase characterisation

LIQUID PHASE	σ_L (mN/m)	CMC (mol/l)	Γ_∞ (mol/cm ²)	K (cm ³ /mol)	ΔG_0 (kJ/mol)
BUTANOL	62.6	-	-	-	-
ANIONIC SURFACTANT	40.7	$5 \cdot 10^{-3}$	$3.52 \cdot 10^{-12}$	$6.25 \cdot 10^9$	-19.62
NON-IONIC SURFACTANT	30.4	$6 \cdot 10^{-4}$	$2.56 \cdot 10^{-12}$	$3.57 \cdot 10^{11}$	-23.90
CATIONIC SURFACTANT	27.4	$2.3 \cdot 10^{-3}$	$3.49 \cdot 10^{-12}$	$9.09 \cdot 10^{10}$	-22.60

b) *Critical Micellar Concentration*

For the three surfactant solutions, the static surface tension is determined for different concentrations. When the surfactant concentration increases, the surface tension tends to decrease until it levels off: the solution is then saturated in surfactants (formation of micells), the Critical Micellar Concentration is reached. The CMCs associated with the surfactants under investigation are reported in Table 2. The lowest CMC is obtained for the non-ionic surfactant and the highest for the anionic surfactant: this result agrees with the molecular size of the surfactants.

As the concentration of the surfactant liquid phases under test is $3.75 \cdot 10^{-3}$ mol/l, only the aqueous solutions of non-ionic and cationic surfactants are saturated.

c) *Characteristic adsorption parameters*

The adsorption of solute molecules at a gas-liquid interface is directly linked to the thermodynamic activity of the dissolved substance, that is to say to its capacity to diffuse from the solution to the interface. This phenomenon is then related to the solute structural parameters (length and shape of the carbon chain, number and location of the hydrophilic groups, ...), which modify the thermodynamic balance of the system.

Several theories have been proposed to model this adsorption equilibrium. In spite of its rather crude and simplified hypotheses, the Langmuir theory is the most widely used; it is expressed in the following equations [18]:

$$s_e = \frac{\Gamma_e}{\Gamma_\infty} = K \frac{C}{1+KC} \quad (1)$$

$$\sigma_{L,0} - \sigma_L \approx RT_a \Gamma_\infty \cdot \log(K) + RT_a \Gamma_\infty \cdot \log(C) \quad (2)$$

$$\Delta G_0 = -RT_a \log(55.5K) \quad (3)$$

where s_e is the surface recovery rate at equilibrium, C the solute concentration in the liquid phase, Γ_∞ the surface concentration when it is saturated, K the adsorption constant at equilibrium, $\sigma_{L,0}$ the surface tension when the solvent is pure, T_a the adsorption temperature and ΔG_0 the free standard energy of adsorption.

When σ_L is plotted as a function of $\log(C)$ (Equation 2), two asymptotes appears: the first one is horizontal ($\sigma_L = \sigma_{L,0}$ when C tends to zero) and the second one has a slope equal to $-RT_a \Gamma_\infty$. Their intersection, which corresponds to a recovery rate s of 0.5, allows the adsorption constant at the equilibrium K to be obtained ($\log(K)=-\log(C)$).

Applied to our surfactants solutions, the curves relating σ_L to $\log(C)$ are shown in Figure 4.

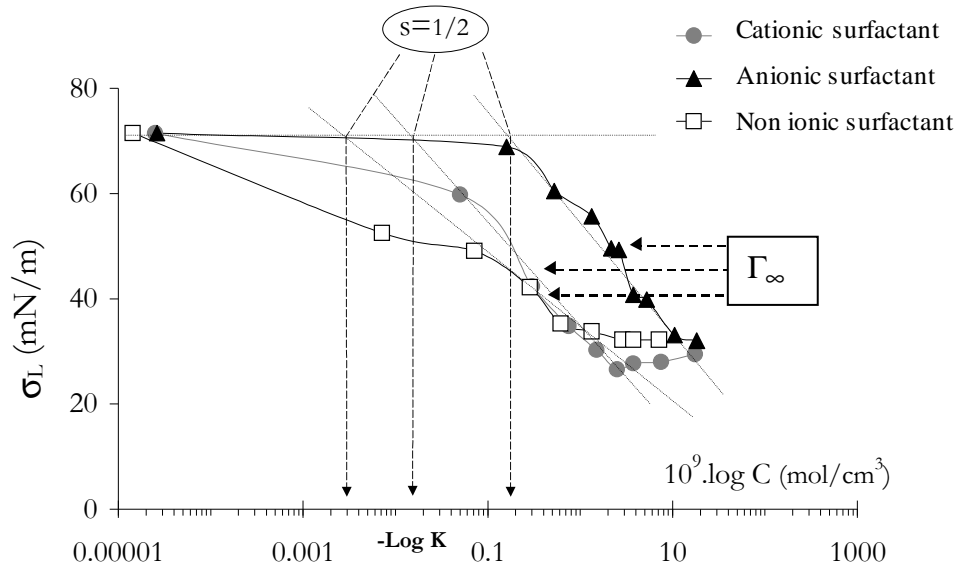


Figure 4. Surface tension as a function of $\log(C)$. Determination of K and Γ_{∞}

Using these curves and Equation 3, the characteristic adsorption parameters K , Γ_{∞} and ΔG_0 can be determined: their values are reported in Table 2. Whatever the surfactants, the surface concentration at the saturation Γ_{∞} and the free standard adsorption energy ΔG_0 are quite similar: this is logical as the three surfactants have the same chemical nature. By contrast, differences appear in terms of adsorption constant at equilibrium K : the largest value is obtained for the non-ionic surfactant and the lowest for the anionic surfactant. Thus, at the adsorption equilibrium, the non-ionic surfactant molecules have a higher affinity towards the interface than the others: their larger size is probably responsible for this result.

Through the previous determinations of K and Γ_{∞} , it is now possible to plot the surface recovery rate at equilibrium s_e as a function of the concentration C (Equation 1, Figure 5).

At the concentration under study ($3.79 \cdot 10^{-9}$ mol/cm³), the surface recovery rate at equilibrium s_e is 1 for the cationic and non-ionic surfactants whereas s_e is 0.7 for the anionic surfactant. This result agrees with the CMC obtained (Table 2): the concentration of study being smaller to the CMC for the anionic surfactant, the interface is not saturated.

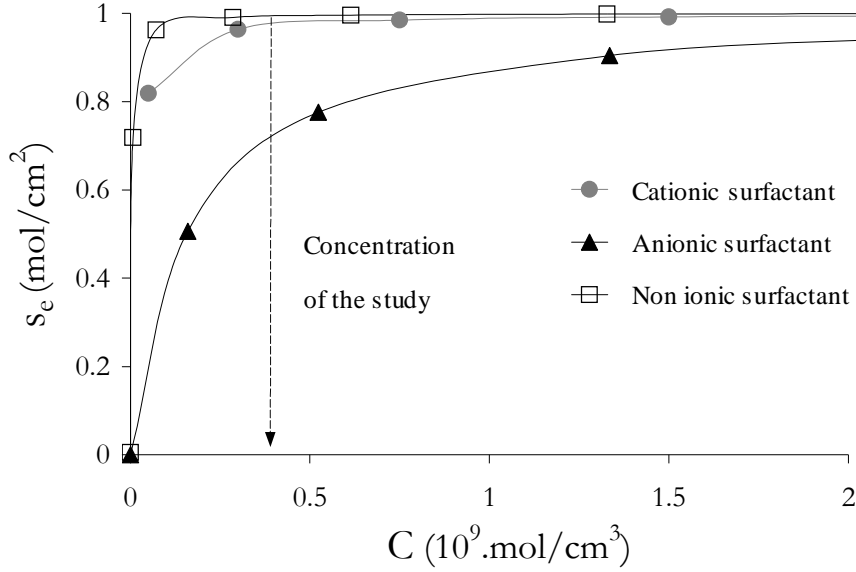


Figure 5. Surface recovery rate at equilibrium s_e as a function of the concentration C

3.2 Dynamic surface tension measurements

The principle of the dynamic method is based on the measurement of the surface tension outside the adsorption equilibrium: the adsorption kinetics is thus taken into account.

In Figure 6 are plotted the surface tension as a function of the time which corresponds to the surface age, for the different surfactant solutions (at 3.75 mmol/l) and for the aqueous solution of butanol. Whatever the liquid phase, the shape of the curves is similar : initially, the surface tension decreases (at varying rates), and afterwards remains constant around a value corresponding to the surface tension at the adsorption equilibrium.

Nevertheless, important differences appear at the level of the initial drop: for the butanol solution, this initial drop is formed almost instantaneously whereas it takes several seconds for the surfactant solutions. These tendencies can be traduced in terms of the slope at the origin and the time necessary to reach a constant surface tension (Table 3). These parameters give information about the molecule's speed towards the bubble surface.

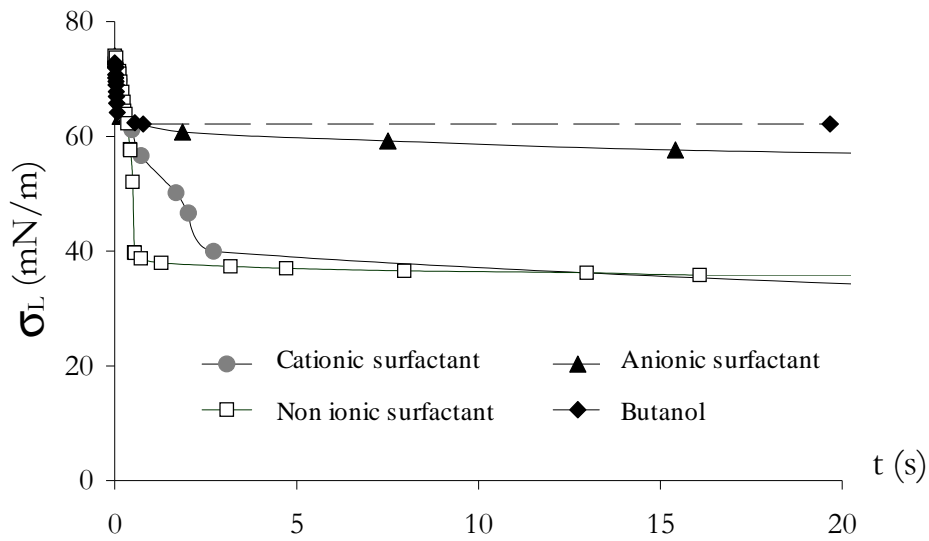


Figure 6. Curves of dynamic surface tension

The fastest diffusion kinetics is obtained for the butanol solution: the surface tension at equilibrium is reached in 0.1 second. For the surfactant solutions, the kinetics are slower: almost 3 seconds are necessary to reach equilibrium with the cationic surfactant.

These different behaviours are directly linked to the nature of the molecules present. With regard to the small molecules of butanol, the surfactant molecules are not able to migrate so fast due to their sizes and their crowding. Consequently, the limiting stage of the phenomenon would probably be the molecules' diffusion towards the interface, and not their own adsorption. Finally, remember that the diffusion stage depends on the concentration: experiments have shown that if the surfactant concentration increases, the slope at the origin increases and the time necessary to reach equilibrium decreases [11].

Table 3. Characteristic parameters of the dynamic surface tension measurements

LIQUID PHASE	SLOPE AT THE ORIGIN (mN/m/s)	TIME NECESSARY TO REACH THE CONSTANT VALUE (s)
ANIONIC SURFACTANT	-66.8	0.2
NON-IONIC SURFACTANT	-43.5	0.8
CATIONIC SURFACTANT	-11.3	2.6
BUTANOL aqueous solution	-147.9	0.08

3.3 Conclusions

The liquid phases under test have been characterised in terms of static and dynamic surface tension and important differences have been highlighted. Figure 7 summarises the main conclusions that can be drawn from this study.

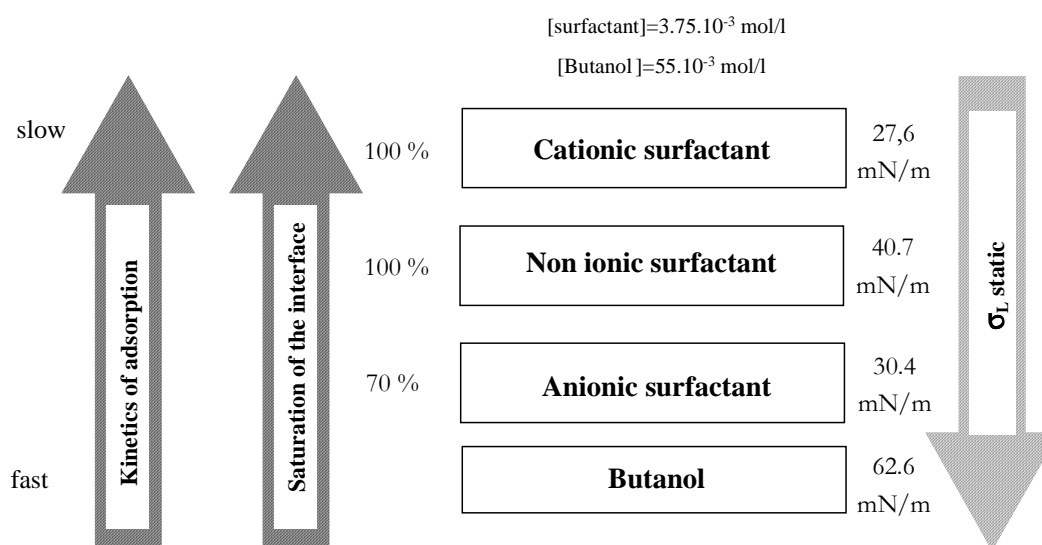


Figure 7. Summary of the principal characteristics of the liquid phases under test

4. Influence of surface tension on the bubbles generated

The aim of this section is to evaluate, to understand and to compare the consequences of a

surface tension modification on the bubbles generated from a rigid orifice and from a flexible orifice.

To this effect, this section will be composed of three parts. Firstly, the impact of surface tension on the dynamics of bubble growth and detachment from both orifices will be examined. The following two parts will be devoted to the results related to the detached bubble diameters and frequencies obtained in the liquid phases under test for the rigid orifice (Part 4.2) and for the flexible orifice (Part 4.3) respectively.

For both orifice types, in order to appreciate the impact of butanol and surfactants, the results will be compared to those obtained in water [13].

4.1 Effects of surface tension on the dynamics of bubble growth and detachment

As in the case of water [13], the dynamics of bubble growth and detachment from rigid and flexible orifices have been integrally studied in the liquid phases under test. Only the main conclusions of the study will be presented here (the detailed results are collected in [11]).

The modification of the surface tension does not modify fundamentally the global characteristics of the dynamics of bubble formation associated with each orifice. As in the case of water, the experiments have shown that:

- whatever the orifice, the bubble growth remains symmetrical about the vertical orifice axis and is composed of two stages (a radial expansion stage and an elongation one);
- the bubble formation at the rigid orifice remains discontinuous (time-out between two successive bubbles) and continuous for the flexible orifice; for the rigid orifice, the gas flow rate supplying the bubble ($q=dV_B/dt$) remains larger than the mean gas flow rate Q_G whereas they remain equal for the flexible orifice;

- the bubble spread over the orifice surface remains more pronounced for the rigid orifice than for the flexible orifice and the spreading dynamics associated with each orifice is conserved;
- for the rigid orifice, the important role of the inertial force in the bubble detachment process is conserved whereas for the flexible orifice, this force remains negligible.

Nevertheless, the modification of the surface tension has local consequences. The variations of several parameters (dy/dt , d^2y/dt^2 , q , d_w , θ) with the bubble growth time can have different effects than was seen in water. In particular, it has been observed that for the rigid orifice, the characteristic parameters depends on the gas flow rate Q_G in the surfactant liquid phases whereas they do not in the case of water.

4.2 Effects of surface tension on the bubbles generated from the rigid orifice

The effects of surface tension on the bubbles generated from the rigid orifice will be appreciated by means of the detached bubble diameters and the bubble frequencies.

a) Bubble diameter

For the rigid orifice, Figure 8 presents the relation between d_B and U_{OR} for the different liquid phases. For hole gas velocities above 6 m/s, the liquid surface tension has no effect on the bubble diameter. Below 6 m/s, the bubble diameter is significantly lower compared to in the case of water. It can be noted that there is now a variation of d_B with U_{OR} , unlike the results in water where the bubble diameter remained constant [13]. The lowest bubble diameters are obtained with the non-ionic surfactant solution ($\sigma_L=30.4$ mN/m), followed by the anionic surfactant solution ($\sigma_L=40.7$ mN/m) and the cationic surfactant solution ($\sigma_L=27.4$ mN/m); the butanol aqueous solution ($\sigma_L=62.6$ mN/m) has no effect on the bubbles generated. These

results confirm the limits of the notion of static surface tension: the smallest bubbles are not obtained with the liquid phase which has the lowest static surface tension.

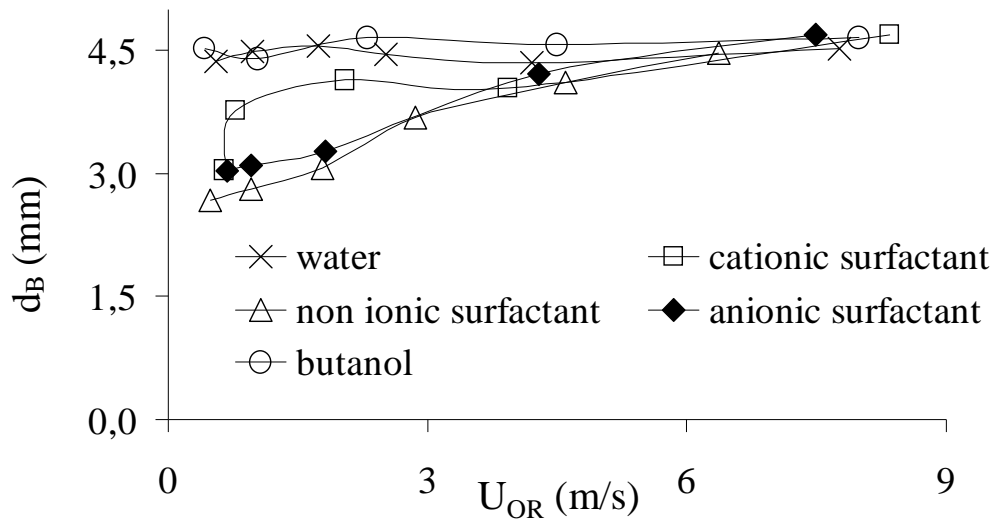


Figure 8. Bubble diameter versus orifice velocity for the rigid orifice

To understand such results, it is necessary to relate them to the measurements of dynamic surface tensions (Section 3.2). Indeed, these measurements have shown that behaviour can differ between the liquid phases in terms of diffusion kinetics and that the time scales of the diffusion kinetics and the bubble formation are comparable. Thanks to these results, some hypotheses can be formulated to explain the results associated with Figure 8:

- the reduction in bubble diameter observed with the non-ionic and anionic surfactants would be linked to their quite fast diffusion kinetics and their low static surface tensions;
- by contrast, the non significant influence of the cationic surfactant would be due to its low diffusion kinetics;
- butanol is a special case: no effect is observed even though its diffusion kinetics is fast.

b) *Bubble frequency*

Figure 9 presents the variations of the bubble frequency with the orifice velocity for the different liquid phases. Note that the bubble frequency is deduced from the sum of the bubble growth time and of the time-out between two successive bubbles.

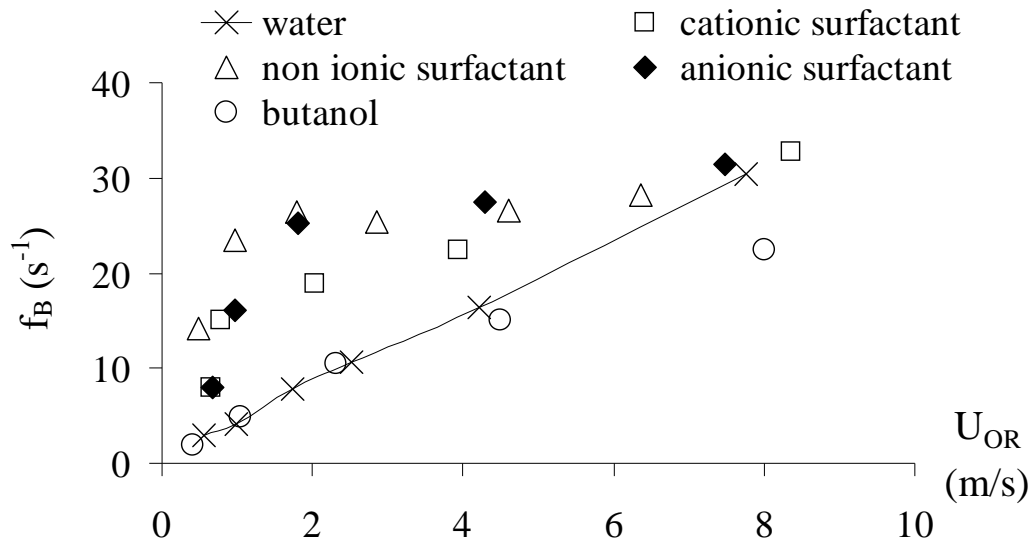


Figure 9. *Bubble frequency versus orifice velocity for the rigid orifice*

The bubble frequencies associated with the butanol solution remain close to those of water. With the surfactant liquid phases, the frequencies are, on average, higher compared to water. This result is the consequence of the fact that, in the presence of surfactants, the time-out between two successive bubbles is lower compared to that in water; in fact, as the liquid molecular cohesion is lower, gas is introduced into the surfactant solutions more easily. Linear in water, the variation of bubble frequency with orifice velocity becomes logarithmic in the surfactant liquid phases. The higher frequencies are obtained with the anionic and non-ionic surfactant solutions.

4.3 Effects of surface tension on the bubbles generated from the flexible orifice

The effects of surface tension on the bubbles generated from the flexible orifice will be evaluated in terms of the detached bubble diameters and the bubble frequencies.

a) Bubble diameter

For the flexible orifice, Figure 10 presents the relation between d_B and U_{OR} , for the different liquid phases.

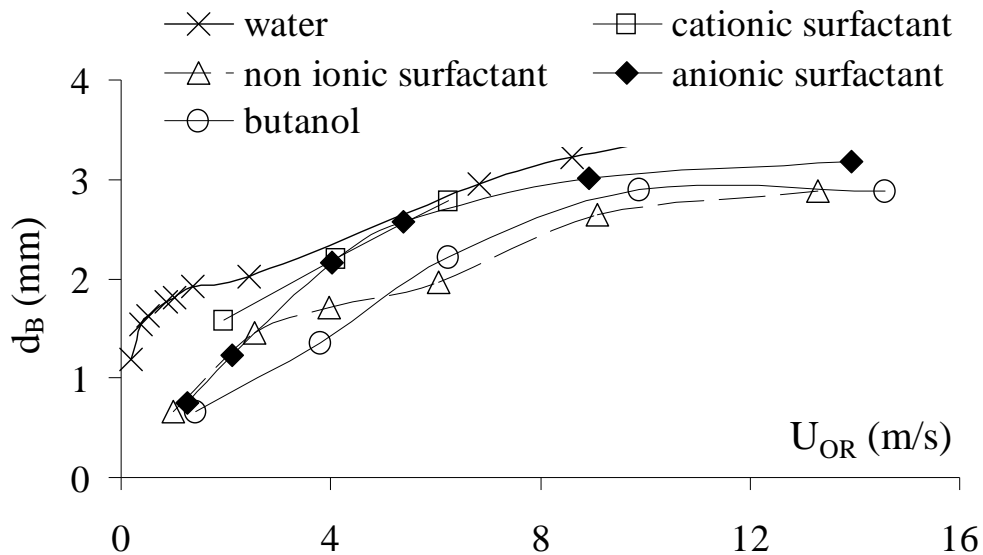


Figure 10. Bubble diameter versus orifice velocity for the flexible orifice

Three general comments can be formulated with regard to Figure 10. Whatever the liquid phases:

- compared to water, the bubble diameters are significantly reduced over the whole hole gas velocity range;
- as with water, the curves have a logarithmic shape;

- below 3 m/s, a special phenomenon occurs which did not exist in water: the bubble jet is divided into two jets (Figure 11). The double jet generates very small bubbles (diameter below 1 mm) with high frequencies (200-1000 s⁻¹). At present, this phenomenon is not yet fully understood. One hypothesis would be based on the fact that, thanks to their high wettability over the orifice surface, these liquid phases would be able to penetrate the gas jet (with low momentum) and so to divide it into two jets: a “liquid bridge” would be formed over the flexible orifice.



Figure 11. Double jet phenomenon

The lowest bubble diameters are obtained with the butanol solution and with the non-ionic surfactant solution, followed by the anionic and cationic surfactant solutions (Figure 10).

Compared to the rigid orifice, some common features appear:

- the low influence of the cationic surfactant on the bubbles generated, which would be due to its slow diffusion kinetics and in spite of its low static surface tension;
- the obvious effects of the anionic and non-ionic surfactants. For these two surfactants, the adsorption equilibrium should be reached; thus, as the surface tension of the anionic surfactant is higher than that of the non-ionic surfactant, the smaller bubbles are logically generated in the non-ionic surfactant liquid phase.

Nevertheless, one essential difference between rigid and flexible orifices has to be highlighted: the butanol solution significantly reduces the bubble sizes formed from the flexible orifice whereas no effect is observed in the case of the rigid orifice (Figure 8). As the solution is not saturated in butanol, the explanation is probably related to the recovery rate of the butanol molecules over the bubble surface. Thanks to the small size of the bubbles generated from the flexible orifice, the butanol molecules would be able to totally cover the bubble surfaces, which would not be possible with the large bubbles generated from the rigid orifice. Some complementary experiments have to be performed to validate or refute this hypothesis.

b) *Bubble frequency*

Figure 12 presents the variations of the bubble frequency with the orifice velocity for the different liquid phases. Note that the bubble frequency is directly deduced from the bubble growth time (continuous process).

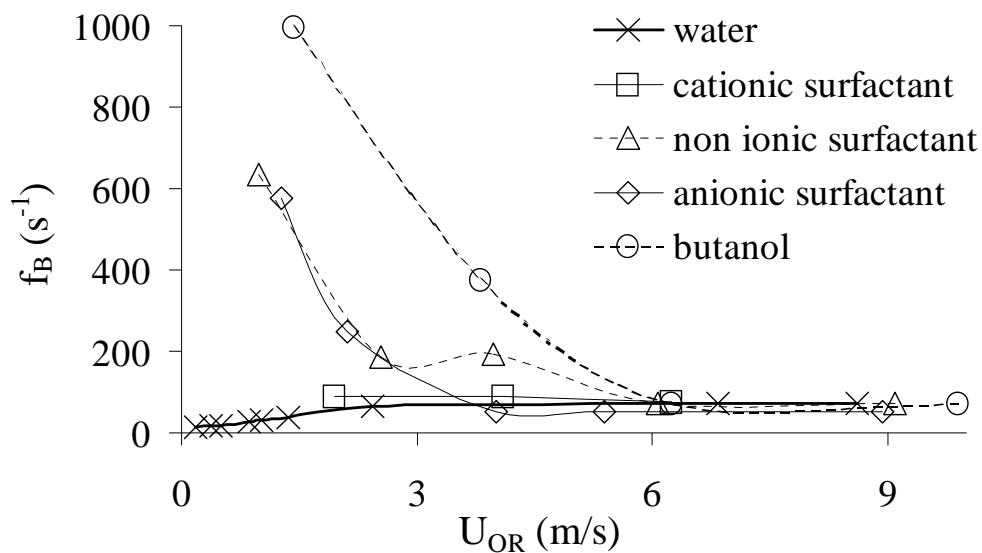


Figure 9. *Bubble frequency versus orifice velocity for the flexible orifice*

For the flexible orifice, whatever the liquid phase, the logarithmic variation observed in the case of water is not seen here. Below $U_{OR} = 4$ m/s, the bubble frequencies are significantly higher than those in water; this is the consequence of the double jet phenomenon previously described. The highest frequencies are obtained with the butanol, followed by the non-ionic, anionic and cationic surfactant solutions. Above 4 m/s, the frequencies are roughly equal to those measured in the case of water: in this orifice velocity range, the modification of the surface tension does not affect the bubble formation frequency.

5. Conclusion

The influence of liquid surface tension on the bubble formation from both rigid and flexible orifice has been investigated. The liquid phases under test were aqueous solutions with butanol or surfactants (cationic, non-ionic and anionic).

Using static and dynamic measurements of surface tension, the liquid phases have been characterised. In addition to their different static surface tensions, the kinetics of adsorption and diffusion of the molecules towards the bubble interface have different behaviours, namely fast for the butanol and slow for the surfactants (more especially for the cationic one).

The study of the impact of surface tension on the bubble formation phenomenon has shown that:

- Whatever the nature of the orifice, the global characteristics of the dynamics of bubble growth and detachment are conserved, even though there are some local consequences.
- For the rigid orifice, compared to water, the bubbles generated in surfactant solutions have smaller sizes, higher frequencies and their characteristics depend on the orifice velocity. No effect of the butanol solution has been observed.
- For the flexible orifice, whatever the liquid phase (butanol included), the variation of the

bubble diameter with the orifice velocity remains logarithmic and, compared to water, smaller bubbles are generated. A double jet phenomenon, not observed in the case of water, appears for orifice velocities below 3 m/s.

Whatever the orifice nature, the most significant effects are not obtained with the liquid phase having the smallest static surface tension. As a consequence, this study proves that the effect of surface tension on the bubbles generated:

- can not be analysed only by the static surface tension,
- depends on whether the bubbles are generated from a rigid orifice or from a flexible orifice.

Such results are directly linked to the kinetics of adsorption and diffusion of the solute molecules. As their time scales are comparable to those of bubble formation, they are no longer negligible. Depending on the orifice nature, as the bubble sizes and frequencies change, the migration of the solute molecules towards the bubble interface, their adsorption and their recovery of the bubble surface are not similar (the example of the butanol is significant).

Even though interesting conclusions have been obtained in this study, complementary research are necessary in the future to analyse in detail these complex phenomena. This is crucial for the understanding of the mass transfer between gas and liquid phases where surfactants are present.

Appendix A: Nomenclature

Roman symbols

- d_B bubble diameter (m)
 d_{OR} equivalent hole diameter (m)
 f_B bubble frequency (s^{-1})

H_L	liquid height (m)
M	molecular mass (g/mol)
R	perfect gas constant ($R=8.314$ J/mol/K)
ΔP_C	critical pressure (minimal pressure required to initiate the bubbling) (Pa)
q	gas flow rate supplying the bubble $q=dV_B/dt$ (m^3/s)
Q_G	mean gas flow rate measured with the soap film meter (m^3/s)
T_B	bubble growth time (s)
U_{OR}	orifice velocity defined as $U_{OR} = Q_G / (\pi d_{OR}^2 / 4)$ (m/s)
V_B	bubble volume (m^3)
V_C	gas chamber volume between the control valve and the orifice (m^3)

Greek symbols

γ_C	wetting critical surface tension of the orifice surface (N/m)
σ_L	liquid surface tension (N/m)
Γ_e	surface concentration when the adsorption equilibrium is reached (mol/m^2)
θ	contact angle between the bubble and the orifice surface ($^\circ$)

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