On the Forced Drainage of Foam

Methods measuring
wet front velocity and liquid hold-up

Sylvain Sonnery

Supervised by Dr P. Martin

School of Chemical Engineering and Analytical Science
University of Manchester

2009

<u>Acknowledgements</u>

Content

1   <u>Introduction to the project</u>

This section of the report introduces the problematic of foam drainage. It also explains how the measurement of the wet front velocity and the liquid hold-up are relevant to study the foam drainage.

1.1   <u>Background</u>

The studies on foam drainage are of significant industrial importance since many technological properties of foam depend on the drainage rate (P.M. Kruglyakov et al, 2007). In fact, uniformity of the foam is important for the designer and since gravitational drainage of the liquid is one mechanism leading to nonuniformity, it is important to characterize the dynamics of drainage (S. A. Koehler et al, 1998).

Foam drainage is a complex physico-chemical hydrodynamic process governed by many simultaneous factors, which are not fully understood. The foam drainage depends not only on the hydrodynamic parameters of the foam system, such as the shape and size of the plateau borders and the gravity but also on the rate of internal foam destruction by the bubble coalescence. The decrease in the average foam dispersion causes the release of excess liquid which slows the establishment of hydrodynamic equilibrium. The liquid drainage along the Plateau borders leads to the increase in the capillary pressure. This effect speeds up the bubble coalescence, resulting in formation of internal holes in the foam body (P.M. Kruglyakov et al, 2007).

1.2   <u>Wet front velocity</u>

Experimentally, it is impossible to measure the foam drainage velocity. Researchers prefer to measure the wet front velocity. This parameter gives a great idea about foam drainage and is easy to measure. The method of forced drainage has been extensively used in the literature to investigate foam drainage as it is a convenient method of assessing the drainage characteristics of the foam (P. Stevenson, 2007).

1.3   <u>Liquid hold-up</u>

The liquid hold is also a relevant parameter characterizing the foam. It is the total liquid fraction present in the foam per unit volume. In a case of free drainage experiment, it reduces with time. The wetter the foam is, the faster the liquid could drain from it. The initial liquid content in foam (after its production) is usually much larger than the liquid content in the foam in hydrostatic equilibrium established after some time from its formation. This change in the liquid content is due to the liquid drainage along the Plateau borders. In addition, the liquid hold-up depends on the height. It will be greater at the bottom than at the top.

On the contrary, if a liquid is continuously added at the top of the body of foam (forced drainage experiment), the liquid hold-up will be the same at each point of the foam after letting the foam equilibrate.

2   <u>Objectives of this project</u>

This section describes the goals to achieve by this research project.

In the case of layout where foam is continuously made and some liquid is added at the top to create a steady reflux, it is impossible to measure the wet front velocity. The only way to determine that is to set up an empiric model to link the wet front velocity to the liquid hold-up, which being easily measured.

The main objective to achieve is to design suitable equipments to measure the liquid hold-up and the wet front velocity. The empiric model will be generated thanks to the data collected.

The accuracy and the repeatability of the model will be studied. However, the influence of parameters such as type of surfactant, its concentration, the air flow rate, the bubbles size or the column diameter will be analyzed.

3   Foam

3.1   Background

Foam is a two-phase system in which a large volume fraction of gas is dispersed as bubbles throughout a continuous liquid matrix (Narsimhan and Wang, 2005 and Weaire and Hutlzer, 1999). Bubbles size may vary from 50 μm to a couple of mm. These bubbles are stabilised by the presence of surfactants. Surfactants make foams compressible and thus avoid the breaking of the thin liquid film between two bubbles. They accumulate preferentially at the liquid-gas interface in order to reduce their free energy.

Table 1 shows the six types of foams according to theirs characteristics.

Type	Characteristics
True	Predominantly gaseous dispersion
Fluid	Predominantly liquid dispersion with enhanced holdup of gas in large portion of liquid
Unstable	Equilibrium state continuously approched
Metastable	Progress to the equilibrium state arrested
Transcient	Stable, a few seconds lifetime
Persistent	Stable, a few hours or days lifetime

Table 1: Types of foams according to their characteristics
Source: (Vardar-Sukan, 1998)

3.2   Foam structure

Generally, foam is classed as wet or dry, depending on the liquid content. In a wet foam (with a liquid volume fraction of 10-20%), the bubbles are approximately spherical, whereas a dry foam (in which the fraction of liquid is less than 10%) consists of roughly polyhedral bubbles (C. J. W. Breward and P. D. Howell, 2001). In dry foam, polyhedral gas cells are separated by thin liquid named 'lamellae'. The common edge of two cells is named 'plateau border'(pb). The connection of four borders forms is referred as 'vertex'.

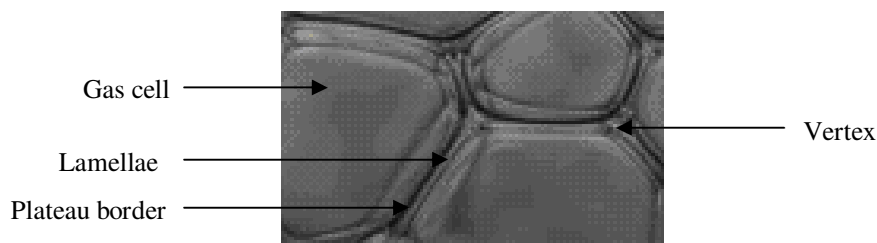Figure 1 illustrates a typical foam structure.

Figure 1 : Foam structure

3.3 Industrial applications

Foams are encountered in diverse industrial processes such as food production, cosmetics, fire fighting, fermentation reactors, mineral processing, effluent treatment and enhanced oil recovery (M. Papara et al, 2008). Chocolate mousse desserts or pouring beer are only a few examples. However, foams can cause many problems for some industries, the main issue being the overflowing of foam.

4 Surfactant

4.1 Background

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water. In foams, surfactants align themselves across the lamellae (figure 2).
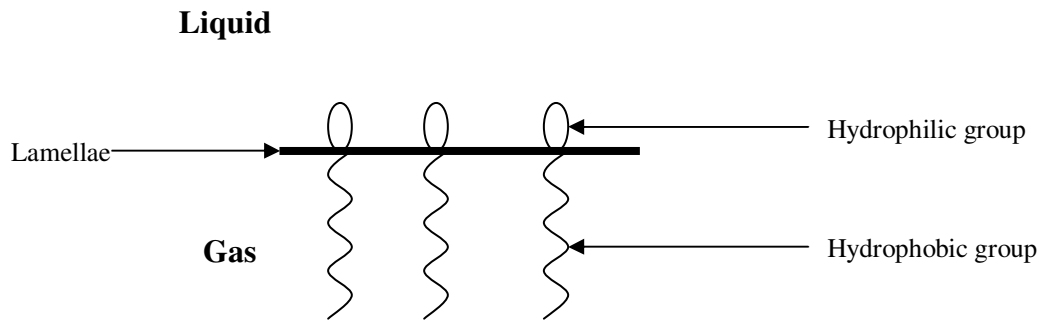

Figure 2 : Surfactant molecule accumulation at a liquid-gas interface
(Source: Winterburn, 2007)

Table 2 shows the four types of surfactants defined regarding to their hydrophilic group:

Types of surfactants	Hydrophilic group
Cationic surfactants	Positively charged
Anionic surfactants	Negatively charged
Zwitterionic	Positively or/and negatively charged (depends on pH)
Non ionic surfactants	Non charged

Table 2 : Types of surfactant according to their hydrophilic group

4.2 Properties

Surfactants reduce the surface tension of water by absorbing at the liquid-gas interface. The surface tension of water provides the necessary wall tension for the formation of bubbles with water. There is a limit to the number of surfactant molecules that can be absorbed to the liquid-gas interface. This concentration is named the Critical Micelle Concentration (CMC).

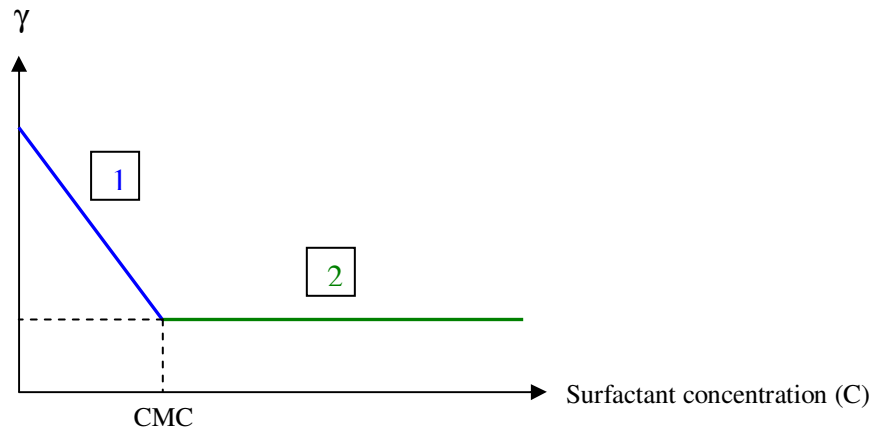Figure 3 shows the general relationship between surfactant concentration and film surface tensions, γ.

Figure 3 : Surface tension vs. surfactant concentration
(Source: Winterburn, 2007)

Part 1 : C<CMC
Surfactants accumulate at the gas-liquid interface.

C=CMC
The interface gas-liquid is fully saturated.

Part 2 : C>CMC
Once the interface is fully saturated, surfactants begin to form micelles. Figure 4 shows how surfactants molecules get organized in a micelle.
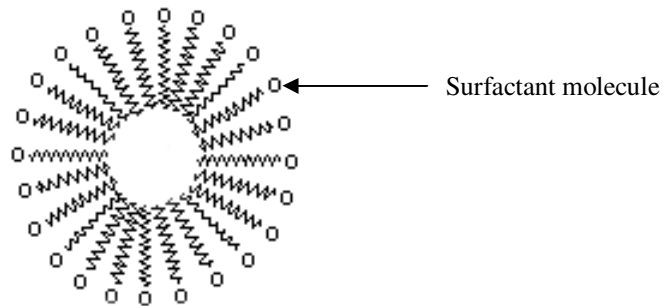

Figure 4 : Micelle

4.3   Industrial applications

Surfactants provide many functions of industrial products:
- Detergents: for cleansing
- Wetting agents: in perms
- Foaming agents: for shampoos, chocolate mousse, beers
- Emulsifiers: in creams and lotions
- Conditioning agents: in skin and hair-care products
- Solubilizers: for perfumes and flavours

4.4   Cetylpyridinium chloride

The wet front velocity and the liquid hold-up velocity will be measured on foams prepared by adding Cetylpyridinium chloride (CPC). It is a cationic quaternary ammonium surfactant. Figure 5 shows the chemical formulae of CPC.
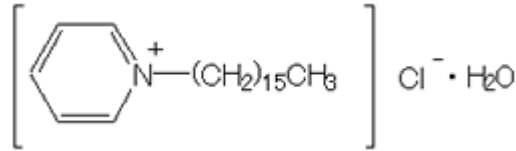

Figure 5 : Cetyl pyridinium chloride monohydrate

Its critical micelle concentration is $9*10^{-4}$ mol/L. It is an antiseptic that has demonstrated its efficiency for killing bacteria and other microorganisms. Moreover, it has been shown to be effective in preventing dental plaque and reducing gingivitis. That is why; it is a compound of some types of mouthwashes and toothpastes (S. Sheen and M. Addy, 2003). It has also been used as an ingredient in certain pesticides.

5   **Experimental techniques**

5.1   Wet front velocity

In the forced drainage experiment, a foam is typically prepared within a straight column by either mechanical agitation or gas sparging. The foam is then allowed to drain under gravity so that it becomes very dry. Typically, the volumetric liquid fraction must become less than 0.01%. Liquid is then added to the top of the column at a given volumetric flow rate so that a wet front travels down the column and there are two distinct zones in the column: a dry zone downstream of the wet front, and a wet zone upstream of the front. The liquid fraction in the wet zone is invariant in height and time. The velocity of the wet front is measured either optically or by measuring the change in electrical conductivity of the foam at stages down the column (P. Stevenson, 2007).

5.1.1   Optically
It may be difficult to follow the wet front at naked eye. The addition of food dye to the liquid applied to the top surface will be helpful to measure the wet front velocity more accurately. Moreover, it is vital to have surfactant in the liquid added at the top or it will "kill" the foam.

5.1.2   Electrical conductivity
Water being conductor, it is easy to follow the wet front by measuring the conductivity of the foam. The conductivity of the wet foam is obviously greater than the conductivity of the dry foam. Figure 6 shows the variation of the conductivity of the foam with time in the case of forced drainage experiment.
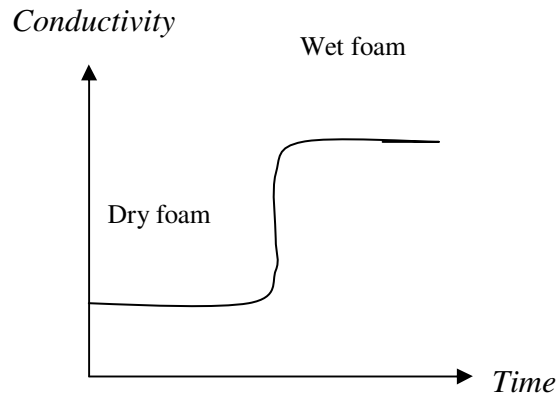
Conductivity

Wet foam

Dry foam

Time

Figure 6 : Electrical conductivity with time (expected graph)

At the beginning, this method had been preferred to the optical one because we assumed that it was more accurate.

5.2   Liquid hold-up

In the case of forced drainage experiment, a foam is prepared in a column. The foam is then allowed to dry for as long as possible before it began to collapse. The volumetric liquid fraction should become less than 0.01%. So the initial liquid hold-up of the foam will be negligible. Liquid is then added to the top of the column at a given volumetric flow rate until the foam reaches a steady state.

5.2.1   Liquid hold-up calculated

It has been demonstrated by a number of workers (D. Weaire et al, 1993 ; S.A. Koehler et al, 1999) that the velocity of the wet front V_w is proportional to a power of the volumetric liquid rate Q applied to the surface, i.e.

$$V_w \propto Q^\alpha \; (1)$$

where α is a dimensionless constant. It is more convenient to work in terms of superficial velocities so the superficial drainage velocity j_d in the foam is

$$j_d = \frac{Q}{A} \; (2)$$

Where A is the cross-sectional area of the column. This superficial velocity occurs in a foam of volumetric liquid fraction ε, which can be determined by using the relationship :

$$\varepsilon = \frac{j_d}{V_w} \; (3)$$

Knowing (2) and (3), the liquid hold-up of the foam can be calculated by using the relationship :

$$\varepsilon = \frac{Q}{A * V_w} \; (4)$$

10

The addition liquid volumetric rate and the cross-sectional area of the column can be easily determined. The wet front velocity is measured according to one of methods described previously.

5.2.2 Liquid hold-up measured

The liquid hold-up of the foam can be easily measured thanks to a sampling tool connected to vacuum. The sampling tool is weighed while empty on the electronic mass balance. Foam is then sucked up from the column for a known time. The foam rate must be measured. So, the volume of foam V_f will be known. The sampling tool is weighed again using the electronic mass balance. The increase in mass is used to calculate the volume of liquid V_l in the foam. It is assumed throughout all experiments that all solutions have a density of 1 g.mL^{-1}

The volumetric liquid fraction ε can be calculated by using the relationship:

$$\varepsilon = \frac{V_l}{V_f} \quad (5)$$

6   Experimental results

6.1   Experiments using Bactericidal Dishwash Liquid as surfactant

6.1.1   Wet front velocity

We used wash liquid as surfactant because the foam prepared with it is very stable. In fact, stable foam is vital to do some forced drainage experiments.

The equipment is composed of :
- An air pump, to generate the foam
- A rotameter, to regulate the air flow rate (from 0 to 5 L/min)
- A sparger, metal tube with holes, to disperse the air within the column
- A peristaltic pump, to add the liquid at the top of the column.
- A distributor to disperse liquid at the top of the column (similar to the sparger)
- A cup, containing surfactant solution composed of 1,25 Vol. % wash liquid and 98,75 Vol. % deionised water.
- A glass column, 50 cm high ; 7,4 of diameter
- Three electrodes and multimetres, to measure the conductance in the body of foam at three different heights.
- Logger Data software, to register on the computer data from mulitimetres

Figure 7 shows the layout of the equipment measuring the wet front velocity.
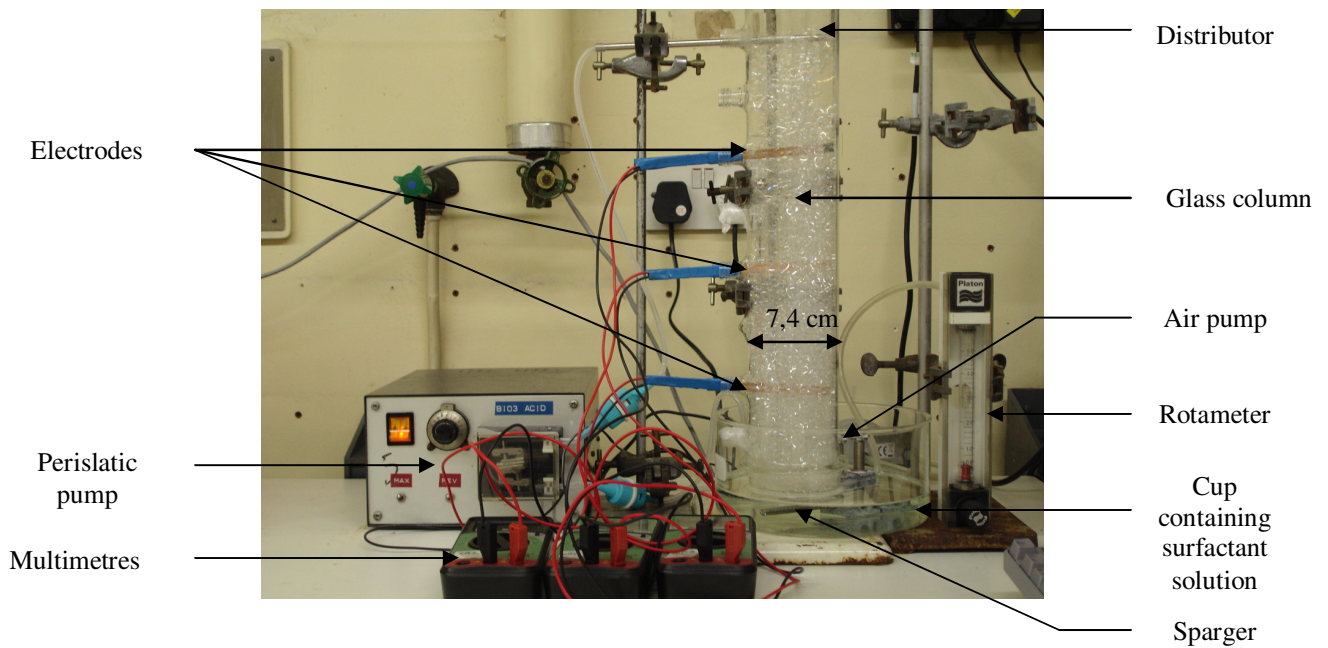
Figure 7 : Layout of the equipment measuring the wet front velocity

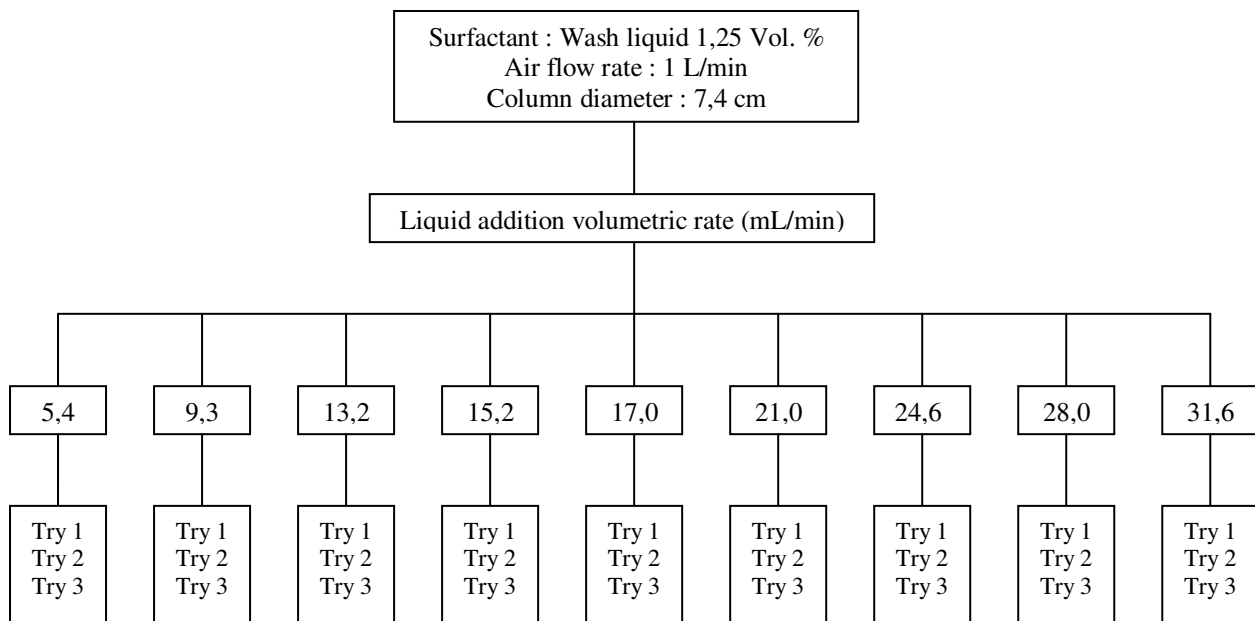Experiments were conducted following the figure 8.

Figure 8 : List of experiments

Each try is done following the figure 9. For all experiments, an initial foam height of 40 cm was generated by bubbling air through the surfactant solution.
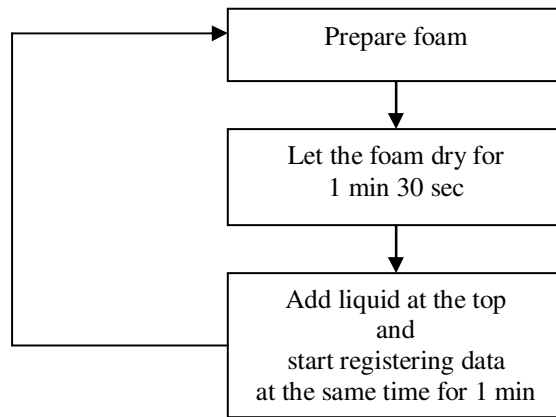
Figure 9 : Experiment step by step

The graph "conductance against time" is slightly different than expected. Indeed, the conductance increases less sharply than expected when the wet front reaches the electrode. We assume that the wet front is not straight but kind of conical. We have to take in part the average wet front when we measure the wet front velocity, which corresponds to the middle of the slope from a low to a high conductance (figure 10).
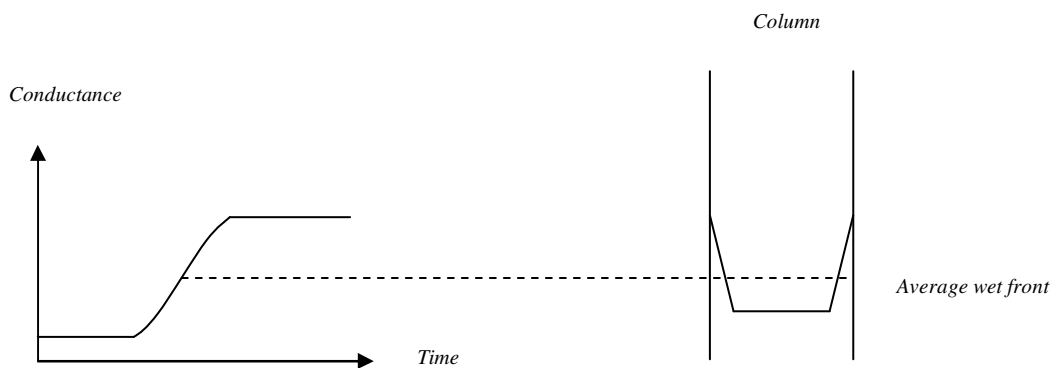
Figure 10 : Average wet front

The wet front velocity is quite different according to the electrode considered. In fact, it was difficult to start adding liquid and registering data at the same time. That is why; the average wet front velocity for each try is obtained by averaging the data from the three electrodes.

Figure 11 shows the variation of the liquid hold-up calculated (equation 4) with the wet front velocity. This graph is obtained from averaging the raw data for the three repeats.

Figure 11 : Variation of the liquid hold-up calculated with the wet front velocity

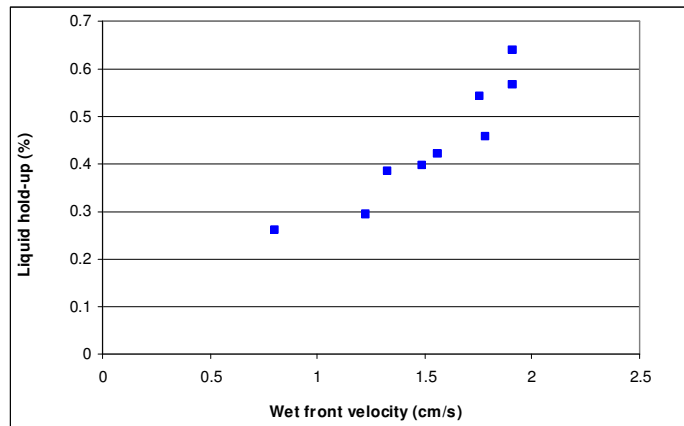As expected, the wet front velocity increases when the foam is wetter. The increase is not steady because of experimental issues.

6.1.2 Liquid hold-up

The equipment is similar as the one used to measure the wet foam velocity. It is composed of :
- An air pump, to generate the foam
- A rotameter, to regulate the air flow rate (from 0 to 5 L/min)
- A sparger, metal tube with holes, to disperse the air within the column
- A peristaltic pump, to add the liquid at the top of the column.
- A distributor to disperse liquid at the top of the column (similar to the sparger)
- A cup, containing surfactant solution composed of 1,25 Vol. % wash liquid and 98,75 Vol. % deionised water.
- A glass column, 50 cm high ; 7,4 of diameter
- A sampling tool, 2,8 mm of diameter.
- A vacuum pump, to suck up foam sample

Figure 12 shows the sampling vessel used to measure the liquid hold-up of the foam.
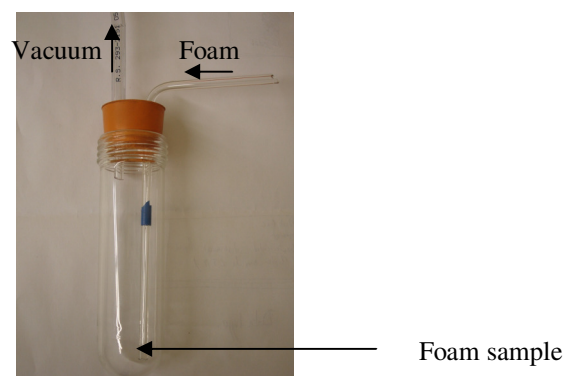

Figure 12 : Sampling vessel

The same set of experiments has been done as in the case of the measurement of the wet front velocity (figure 8).

Each try is done following the figure 13. For all experiments, an initial foam height of 40 cm was prepared by bubbling air through the surfactant solution.
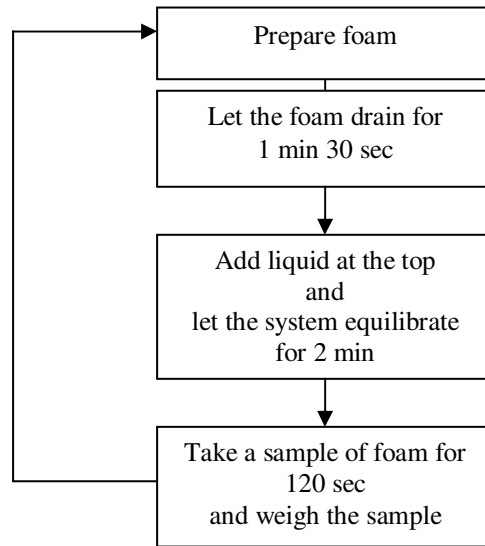
```
        ┌──────────────────────────┐
   ┌───▶│      Prepare foam        │
   │    └──────────────────────────┘
   │                 │
   │                 ▼
   │    ┌──────────────────────────┐
   │    │   Let the foam drain for  │
   │    │       1 min 30 sec        │
   │    └──────────────────────────┘
   │                 │
   │                 ▼
   │    ┌──────────────────────────┐
   │    │    Add liquid at the top  │
   │    │            and            │
   │    │  let the system equilibrate│
   │    │         for 2 min         │
   │    └──────────────────────────┘
   │                 │
   │                 ▼
   │    ┌──────────────────────────┐
   │    │  Take a sample of foam for │
   │    │          120 sec          │
   └────│    and weigh the sample   │
        └──────────────────────────┘
```

Figure 13 : Experiment step by step

Figure 14 shows the variation of the liquid hold-up measured with the wet front velocity. This graph is obtained from averaging the raw data for the three repeats. On this graph is also shown the liquid hold up calculated thanks to the previous measurement of the wet front velocity (equation 4).
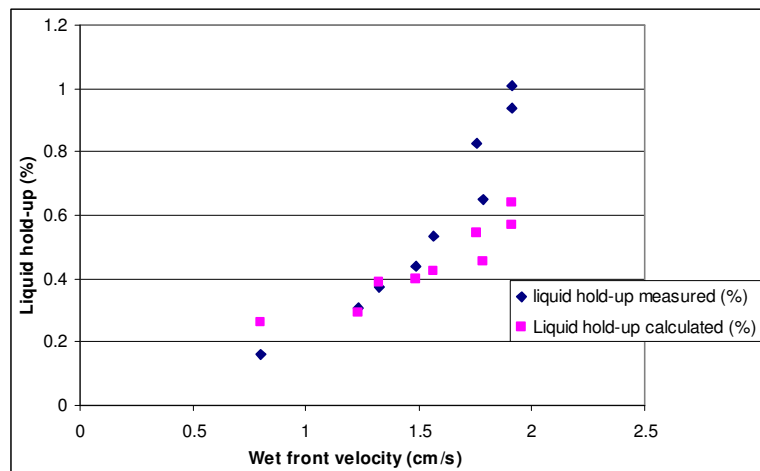

Figure 14 : Variation of the liquid hold-up with the wet front velocity

Liquid hold-up calculated and measured are quite different. In fact, the liquid hold-up measured is much greater than the liquid hold-up calculated for high liquid addition flow rate. The differences between the two ways must be explained and the most accurate methods must be identified.

As explaining previously, it was difficult to accurately measure the wet front velocity with electrodes. That is why; a new set of experiments was carried out to measure the wet front velocity by adding a food colouring instead of following the conductance.

Figure 15 shows the liquid hold up calculated with the two sets of values of wet front velocity as well as the liquid hold-up measured.
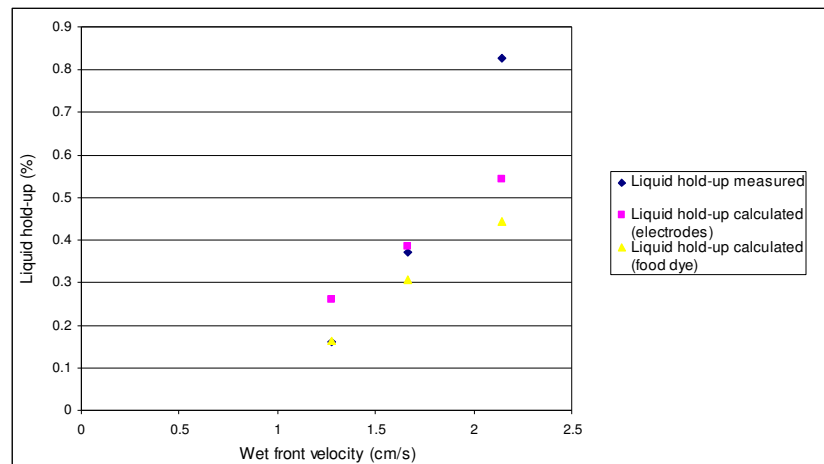

Figure 15 : Electrodes vs. Food dye

The liquid hold-up calculated with the two sets of value of wet front velocity were slightly different. However, it could not explain the difference with the liquid hold-up measured.

Another hypothesis was that the foam was not enough dry before adding liquid. In this case, the liquid hold-up measured would correspond to the liquid initially present in the foam plus the liquid added. A set of experiments was led to measure the initial liquid hold-up. It was less than 0,01 %. This value was negligible compared to the values obtained in the case of forced drainage experiments.

Some extra liquid could be sucked up while taking a foam sample. This could explain the hypothetic overestimation of the liquid hold-up measured. To avoid sucking up some extra liquid, we had to take a sample for a couple of seconds instead of 120 seconds. Experimentally, it is impossible to sharply increase the rate at which the foam was sucked up. So, a sampling tool with a wider diameter had to be used (6,8 mm instead of 2,8 mm).

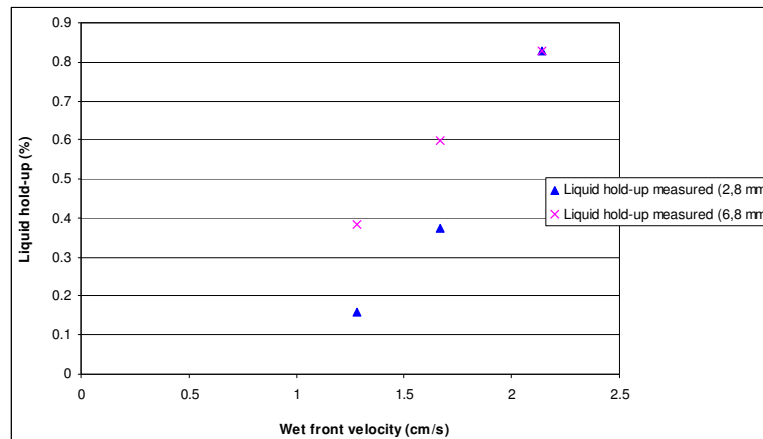Figures 16 shows the liquid hold up measured with the two sampling vessels.

Figure 16 : Sampling vessels - 2,8 mm of diameter vs. 6,8 mm of diameter

Values obtained with the two sampling tools were different. These experiments showed that the method measuring the liquid hold-up was not reliable. In fact, whatever the diameter of the sampling tool, the liquid hold-up measured must be exactly the same. However, it could be interesting to evaluate how repeatable this method was. We decided to change the rate at which the foam was sucked up for each set of experiments in order to evaluate how it could influence the values measured.

Figure 17 shows the liquid hold-up measured with a same sampling vessel at three different rates at which the foam is sucked up.
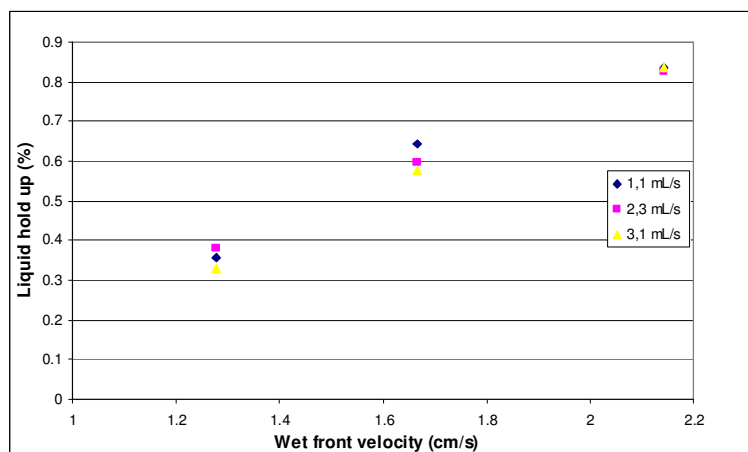

**Figure 17 : Effects of the rate at which the foam is sucked up
on the measurement of the liquid hold-up**

Values measured were slightly different. It could be interesting to determine how repeatable this method was by calculating the coefficient of variation (CV). It is defined as the ratio of the standard deviation σ to the mean μ:

$$CV = \frac{\sigma}{\mu} *100 \ (\%) \ (6)$$

17

Table 3 shows the coefficient of variation for the three liquid addition flow rates tested.

	5,4 mL/min	13,2 mL/min	24,6 mL/min
CV (%)	7,2	5,6	0,5

Table 3 : Coefficients of variation

The coefficients of variation are less than 10 %. In conclusion, although this method is not accurate, we showed that it is repeatable. Nevertheless, we were unable to explain why the liquid hold-up measured tends to be overestimated.

Afterwards, we decided the right way to measure the liquid hold-up was by calculation. We studied the influence of parameters such as the column diameter to check the accuracy of this method. Two set of experiments were carried out using two different glass columns. Table 4 shows the characteristics of these columns.

	Column 1	Column 2
Diameter (cm)	5,3	7,4
Cross-sectional area (cm^2)	22,1	43,0

Table 4 : Characteristics of columns

Figure 18 shows the variation of the liquid hold-up calculated with the wet front velocity. This graph is obtained from averaging the raw data for the three repeats.
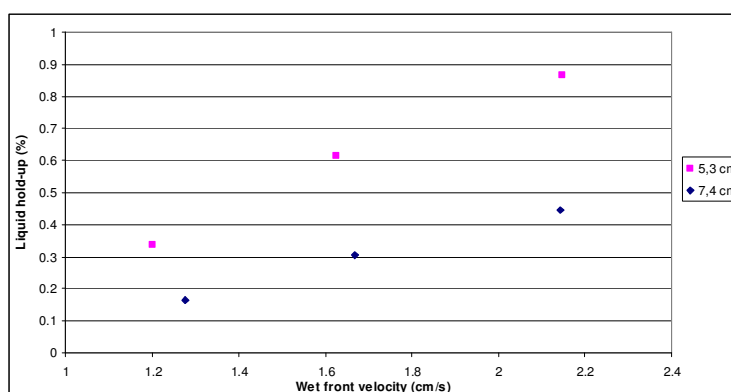

Figure 18 : Glass columns – 7,4 cm of diameter Vs. 5,3 cm of diameter

The liquid hold-up is twice greater for a cross-sectional twice smaller. This demonstrates the accuracy of this method and confirms the choice of this method. It can be used as a reference method.

6.2 Experiments using Cetylpyridinium chloride as surfactant

Our empiric model will be used by Dr Helen Dutton to determine the wet front velocity in her experiments. Indeed, she continuously makes foam and adds at the top of the column some liquid to create a steady reflux but she does not know the wet front velocity in the body of foam.

We had to work in the same conditions as her if we wanted our model to provide accurate data. The main parameters that could have an effect on the wet front velocity were the bubbles size and the column diameter. Bubbles size depends on the surfactant used, its concentration, the holes size of the sparger and the air flow rate. We had a column with a similar diameter. A sparger has been manufactured with the same holes size. Dr Dutton uses Cetylpyridinium chloride as surfactant at 0,5 mmol/L, which is below the Critical Micelle Concentration. She chose CPC because it makes foam easy to break. On the contrary, the foam must be enough stable to do some forced drainage experiments. We had to increase the concentration to 18 mmol/L to prepare a stable foam. This fact has been taken in part when we analyzed our results. In fact, we assumed that the wet front velocity strongly depends on the surfactant concentration.

All the experiments were carried out using the layout previously described. However, it seemed that it was quite difficult to start adding liquid and registering data at the same time. That is why; we chose to use only one electrode to measure the wet front velocity. Experiments were conducted following the figure 19.
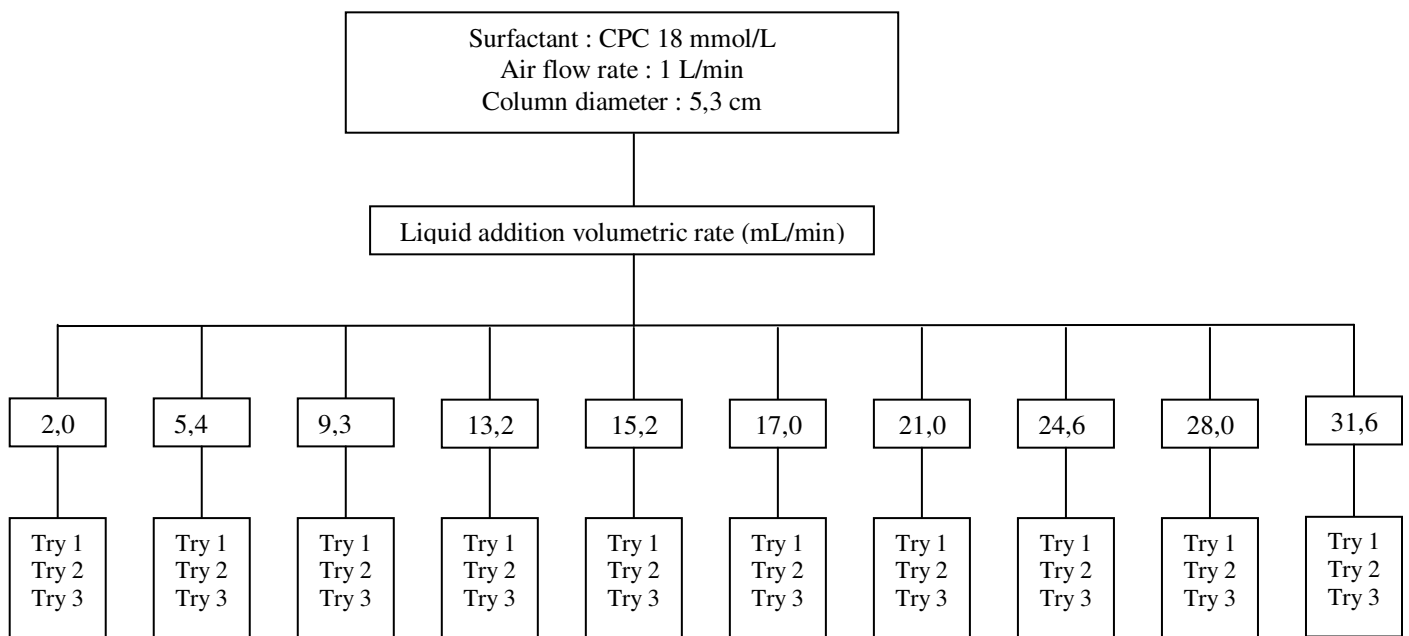

Figure 19 : List of experiments

Figure 20 shows the variation of the liquid hold-up measured with the wet front velocity. This graph is obtained from averaging the raw data for the three repeats. On this graph is also shown the error bars. It was impossible to determine the errors bars for each liquid addition flow rate because the method is not precise enough.
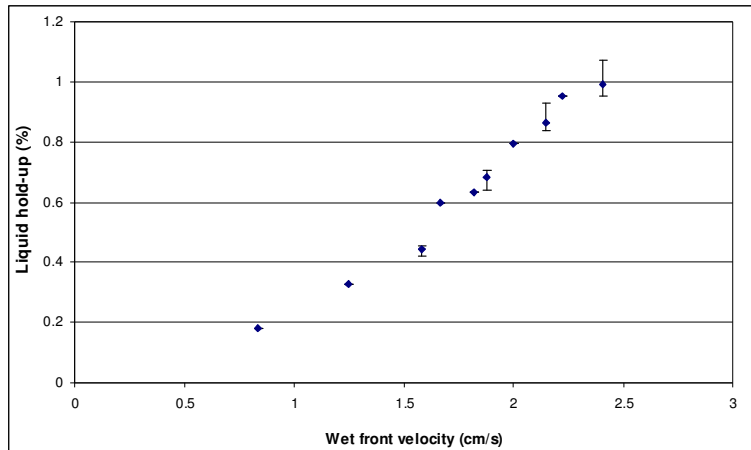
Figure 20 : Empiric model

This graph allows to determine the wet front velocity in the body of foam, knowing the liquid hold-up of the foam. However, it will be more convenient to plot the wet front velocity against the liquid hold-up. It turned out that the curve is kind of logarithmic. Therefore, we used a logarithmic scale to obtain a linear model.
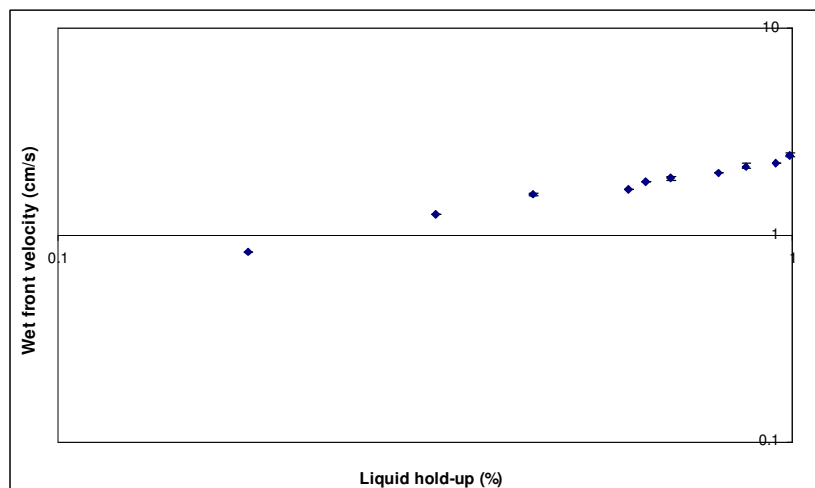

Figure 21 : Linear model

This model permits to determine the wet front velocity, knowing the liquid hold-up of the foam. It is accurate only in the same experimental conditions:
- Surfactant : Cetylpyridinium chloride at 18 mmol/L
- Column diameter : 5, 3 cm
- Air flow rate : 1L/min

7   Conclusion

7.1   Achievement of objectives

The objectives of this project were defined in chapter 2.

The main objective of this project was to generate an empiric model to determine the wet front velocity, knowing the liquid hold up of the foam. This goal has been successfully achieved. However, the main issue was to accurately measure the liquid hold-up.

It turned out that the method, where a sample foam is taken, is not accurate. In the case of forced drainage experiments, the liquid hold-up can be determined by using the equation (4). The case where some foam is continuously made and some liquid is added at the top to create a steady reflux is much trickier. In fact, the liquid hold-up depends on the height. However, an average value can be determined, knowing the air flow rate and the volumetric rate at which the liquid is added at the top. The wet front velocity calculated thanks to the empiric model will be an average value.

This model is quite limited. In fact, it can be used only in the same experimental conditions:

- Surfactant : composition, concentration
- Air flow rate
- Column diameter

Only the effect of the column diameter has been studied in this project.

7.2   Further work

For further experiments, studying the effect of the surfactant concentration will be a useful starting point. In fact, the concentration of the surfactant is expected to have a great effect on the wet front velocity (D. Weaire et al, 1993 ; S.A. Koehler et al, 1999). The effect of the air flow rate can be also studied.

8   <u>References</u>

Verbist, G. and Weaire, D. (1994) Soluble Model for foam Drainage, *Europhys. Lett.* **26**(8), 631-634

Koehler, S. A. et al (1998) Dynamics of foam drainage, *Physical Review*, **58**(2), 2097-2106

Koehler, S.A. et al (2004) Foam drainage on the microscale, *Journal of Colloid and Interface Science*, **276,** 439-449

Kruglyakov, P.M. et al (2008) Foam drainage, *Journal of Colloid and Interface Science*, **13,** 163-170

Safouane, M. et al (2008) Aqueous foam drainage : Role of the rheology of the foaming fluid, *J. Phys. IV*, **11**, 275-280

Koehler, S.A. et al (1999) Liquid Flow through Aqueous Foams : The Node-Dominated Foam Drainage Equation, *Physical Review Letters*, **82**(21), 4232-4235

Verbist, G. and Weaire, D. (1995) Measurement of foam drainage using AC conductivity, *Physical Review Letters*, **82**(21), 217-222

Stevenson, P., (2007) On the forced drainage of foam, *Colloids and Surfaces A*, **305,** 1-9

Weaire, D. et al, (1993) Steady-State Drainage of an Aqueous Foam, *Physical Review Letters,* **71**(16), 2670-2674

Winterburn, J. (2007) Sound Methods of Breaking Foam

Bourne, T. (2008) Recovering Bio-Products From Foams

Cozas, M. (2008) Setup of a method to study foams.

Nomenclature

Q	Volumetric liquid rate (mL/min)
V_w	Velocity of wet front (cm/s)
j_d	Superficial drainage velocity (cm/s)
A	cross-sectional area of the column (cm^2)
V_f	Volume of foam (cm^3)
V_l	Volume of liquid (cm^3)

Greek letters

γ	Surface tension (N/m)
ε	Volumetric liquid fraction or liquid hold-up (%)
σ	Standard deviation
μ	Mean

Subscript

C	Surfactant concentration
pb	Plateau border
CMC	Critical Micelle Concentration
CPC	Cetylpyridinium Chloride
CV	Coefficient of Variation