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## **EFFECT OF HUMIC SUBSTANCES AND PARTICLES ON BUBBLE COALESCENCE AND FOAM STABILITY IN RELATION TO DISSOLVED AIR FLOTATION PROCESSES**

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In this paper the effect of humic substances (natural surfactants), electrolytes and solid particles on bubble coalescence, and as a consequence on froth stability, have been investigated. We formed two bubbles of equal size and forced them to collide using a novel experimental apparatus. The interactions were recorded by a high-speed camera, the images of which helped to determine the coalescence frequency and the coalescence time, as well as the mechanisms of the interactions. Two types of humic substances were used, along with three different electrolytes. Humic substances appeared to have a considerable effect on bubble coalescence, while the effect of electrolytes was minimal. Moderate and high hydrophobic glass spheres were used between two bubbles. Very hydrophobic spheres promoted fast bubble coalescence, while moderate hydrophobic spheres had no effect. We present data of coalescence frequency and time, as well as images of the coalescence events. The coalescence frequency was used to validate a parameter,  $P_f$ , known as the film failure frequency, used in a simulation model to predict foam height in a gas-sparged vessel. Predictions determined using  $P_f$  were then validated by experimentation.

*Key words: bubbles, coalescence, flotation, surfactants, electrolytes, particles, froths, foams*

### **INTRODUCTION**

The formation and stability of froth is important in many industrial processes. For instance, in flotation processes, during which air bubbles capture solid particles from the bulk liquid and subsequently rise to the surface, where they form a froth layer. A great deal of work has been published attempting to establish the influence of various parameters on this phenomenon, such as the characteristics of the surfactants,

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electrolytes and solid particles (Bhakta and Ruckenstein, 1997; Darton and Sun, 1999; Dippenaar, 1982a; Pugh, 1996; Ross, 1991). With an increased interest in the application of dissolved air flotation (DAF) to the purification of drinking water, a fundamental understanding of the effect of various operational conditions on froth formation and stability is vital for process optimisation and control, since the efficiency of this process depends heavily on this phenomenon.

With regards to drinking-water treatment, DAF was first used in 1965 in Finland (Heinänen et al., 1995) and since 1970 in South Africa (Haarhoff and van Vuuren, 1995). It is now widely used in many more countries, such as Belgium and The Netherlands (van Puffelen et al., 1995), in Asia and Australia (Edzwald, 1995), while it is an emerging technology in North America (Schmidt et al., 1995; Nickols et al., 1995; Adkins, 1997). In the UK, DAF plants appeared in the 1970's, initially at a limited number of sites. Nowadays, the number of DAF plants in the UK is probably more than 90 (Gregory, 1997). DAF is very effective for natural waters rich in algae and humic substances (coloured waters) and is very important because of existing and proposed regulations that require filtration of surface waters and increased removal of protozoa cysts such as *Cryptosporidium* and *Giardia* (Edzwald, 1995).

This paper is concerned with the influence of the basic constituents of water in DAF tanks in the drinking-water purification treatment on the formation and stability of froth. These constituents include humic substances, electrolytes and solid particles.

Humic substances (HSs) are a form of the natural organic matter in water, accounting for 40% - 90% of the dissolved organic carbon. They are high molecular weight, coloured, polyelectrolytic, organic acids (Thurman, 1985). Usually, they are divided into two fractions: (a) the fulvic acid, which is of lower molecular weight (500-2000) and soluble in water under all pH, and (b) the humic acid, which is of higher molecular weight (2000 – 5000) and it is not soluble in water under acidic conditions ( $\text{pH} < 2$ ) but is soluble at higher pH values. HSs are important constituents of water because they appear to be present in all natural waters and play a vital role in determining many aquatic processes. The concentration of HSs varies for different natural waters; streams, rivers, and lakes contain from 0.5 to 4.0 mgC/l, and coloured rivers and lakes have much larger concentrations of HSs, from 10 to 30 mgC/l. HSs, as with other natural organic compounds, possess hydrophobic and hydrophilic functional groups. As a result they reduce the surface tension of water and exhibit similar to synthetic surfactants, surface activity (Anderson et al., 1995), and this is the reason why people refer to them as natural surfactants.

Electrolytes are added in natural water just before the water to enter the DAF tank, in order to encourage the particulate matter contained in it to coagulate and flocculate in larger particles. In the literature there are some papers demonstrating the inhibition effect of electrolytes on bubble coalescence (Oolman T.O. and Blanch, 1986; Lessard and Zieminski, 1971; Pashley and Craig, 1997; Deschenes et al., 1998, Laskowski et al., 2003), though there is not a clear explanation for this effect.

Solid particles, that is the matter that its removal from drinking water is aimed, can also play a role on froth stability. In fact, previous workers studying froth stability in the presence of particles have found that particles can promote or inhibit froth stability (Dippenaar, 1982a; Dippenaar, 1982b; Johansson and Pugh, 1992; Spyridopoulos and Simons, 2004). It can be said that the shape, the number, and, perhaps most importantly, the hydrophobicity of the particles play a crucial role on the bubble coalescence and the subsequent phenomenon of froth stability. Dippenaar (1982a) found that a particle caused the rupture of the liquid film -formed between two liquid-air interfaces- when the two three-phase lines were forced to migrate to the same point on the particle. Smooth spherical particles with a contact angle of  $\theta > 90^\circ$  ruptured the liquid films when the films thinned for the particles to bridge them. Particles with irregular shapes could rupture the films even when  $\theta < 90^\circ$ . Johansson and Pugh (1992) found that particles in the size range 26 - 40  $\mu\text{m}$ , showed the following behaviour:

- For less hydrophobic particles ( $\theta < 40^\circ$ ), there was little influence on froth stability.
- Particles of intermediate hydrophobicity increased froth stability.
- Particles of high hydrophobicity ( $\theta > 80^\circ$ ) the particles ruptured the liquid film.

We have studied the effect of HSs, electrolytes and solid particles on froth formation and stability by conducting bubble coalescence experiments using a novel instrument, known as a Micro-Force Balance (MFB), developed in our laboratory. Bubbles of diameter up to 1 mm are grown on opposing nozzles inside a glass cell filled with an aquatic solution. The bubbles are brought together by the expansion of a piezoelectric tube. The rate of expansion and the resulting collision are controlled by software, which control the frequency and the value of the signals sent to a micromanipulator. For the cases where the HSs and the electrolytes were examined, we have observed the conditions under which the bubbles coalesce, e.g. coalescence frequency, type and concentration of HS/electrolyte, and bubble size. For the cases where we had coalescence, we measured the coalescence time, using high-speed video. The effect of solid particles on bubble coalescence was conducted by using glass spheres of different degrees of hydrophobicity. By attaching a glass sphere to the bottom of a bubble and pushing another bubble underneath we could record the particle influence on bubble coalescence. In this paper we present data of coalescence frequency and coalescence time, as well as images of the coalescence events.

To describe foam or froth stability, the frequency of failure of films must be described as a function of any number of applicable variables. In a two-phase system, the three most important variables are the chemical conditions (amount and type of surfactant in the films), the radius of curvature of the Plateau borders and vertices,  $r_{\text{PB}}$ , (and hence the pressure exerted on the films) and the size of the films themselves (which is directly related to bubble size,  $r_{\text{bubble}}$ ).

In an earlier paper, we have defined the film failure frequency,  $P_f$ , to describe film failure, where  $P_f = (\text{average lifetime of a film})^{-1} = f(r_{\text{PB}}, r_{\text{bubble}}, \text{chemical conditions})$

(Cilliers et al., 2003). Coalescence is the failure of the film (lamella) between two neighbouring bubbles and results in the formation of a single, larger bubble. Coalescence results in a loss of lamella surface, and of Plateau border length. The rate of coalescence is determined by the stability of lamellae between bubbles in the froth. Immediately after the film between two bubbles has failed, surface tension will straighten the remaining lamellae. Some of the liquid from the lost Plateau border will remain trapped in the single lamella that is formed out of the two lamellae that existed before. Due to the relatively sharp curvatures associated with the relic of the previously existing Plateau border, this liquid will rapidly enter and thickening the new lamella. Coalescence therefore wets the new, larger film that is formed. It is possible that the lamella straightening will precipitate failure and lead to cascades of coalescence events. This can sometimes be observed in practice.

While the film failure frequency function may be obtained purely by experimental means, it is useful to consider the functional forms for  $P_f$  suggested by different coalescence mechanisms. The two dominant mechanisms are; the time taken for the film to thin beyond its failure limit and the mechanical vibrations required to rupture a film that is at its equilibrium thickness. The first results in an expression for  $P_f$  shown in equation (1), whilst the second results in two slightly different expressions depending on the nature of the disturbances acting on the film. The expressions are discussed in detail in Neethling et al. (2002). In this paper we show how experimental measurement of  $P_f$  indicated that the former theory best describes foam stability.

$$P_f = \frac{K_1}{r_{\text{bubble}}^n} \times \left( \frac{1}{r_{\text{PB}}} - \frac{1}{r_{\text{PB(Critical)}}} \right) \quad (1)$$

where  $n$  takes a value between 1 and 2 and  $K_1$  is proportional to the fluid viscosity, but also depends on surface chemistry since it affects the film thickness at which rapid, van der Waal's induced failure occurs.

## EXPERIMENTAL

### BUBBLE COALESCENCE MEASUREMENTS

#### Materials

A sample of fulvic acid (FA) extracted from a sitka Spruce stand at Rumster in Caithness, UK, was provided by Thames Water Plc (Kempton, UK), one of the major water companies of the UK and collaborators in this project. A second sample of FA, from the Cairgorms region in Scotland, was purchased from the Macaulay Institute (Aberdeen, UK). Thames Water also provided two samples of different molecular weight polymaleic acid (PMA), which is a synthetic polymer that resembles humic and fulvic acids. The samples were stored in glass containers inside a glass desiccator, due to the tendency of the HSs to absorb water from the atmosphere.

Solutions of the HSs were prepared by dissolving a specific quantity of the sample in AnalaR-grade water (BDH, Dorset, UK). Though the HSs were supposed to be soluble in water (since they were FA), they contained traces of non-soluble matter, such as silica, which had to be removed by passing the solutions through a filter paper with pore size of 0.2  $\mu\text{m}$ . The pH of the aquatic solutions was adjusted to 5.0-5.5, the pH usually encountered in drinking-water treatment, using a few drops of (for acidic solutions) NaOH 0.1N or (for basic solutions) HCl 0.1N (BDH, Dorset, UK).

Three electrolytes, potassium chloride (KCl), calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) and lithium chloride (LiCl), were purchased from BDH Laboratories Supplies (Poole, UK) and were of AnalaR grade. The solutions of the electrolytes were prepared by simply dissolving the salt in AnalaR-grade water, with no further treatment.

Repelcote VS was purchased from BDH (Dorset, UK). Methanol and ethanol were obtained from Fluka (Dorset, UK). Lead-glass spheres were purchased from Plowden & Thompson Ltd (, UK), with diameters in the range 20-100  $\mu\text{m}$ . Microscope slides were purchased from BDH (Dorset, UK).

#### **Measurement of surface tension**

The measurements of the surface tension of the HS solutions were conducted with the Wilhelmy-plate method, using a Krüss K-12 tensiometer (Krüss GmbH, Hamburg, Germany). For each concentration and sample, three measurements were taken and the average taken as the surface tension of the solution.

#### **Silanisation of spheres**

The spheres were cleaned by immersing them in a 1:1 MeOH-HCl solution for 30 mins and thoroughly rinsing with distilled water. This procedure has been found to produce fairly clean glass surfaces (Cras et al., 1999). Finally, the spheres were rinsed with AnalaR-grade water and were dried in a furnace for 24 hrs. The spheres were hydrophobised by reaction in a silanising solution, Repelcote VS. The detailed procedure is described elsewhere (Fairbrother, 1998). The spheres remained immersed for ten minutes in the solution and subsequently were rinsed with EtOH before placing in the furnace at 150 °C for 24 hrs to dry.

#### **Measurement of contact angles**

The contact angles of the glass spheres in AnalaR water were determined by conducting the measurements on glass slides that had undergone the same procedure with the glass spheres. Prior to measurement, the slides were rinsed in AnalaR water and dried in an oven. The measurements were carried out with a Krüss K-12 tensiometer GmbH (Hamburg, Germany), which makes use of the Wilhelmy-plate method. With this instrument, the values of the advancing and the receding contact angles were taken. The contact angle of the solid surface was taken the average of these values. For each glass sphere (untreated/silanised/glass type) three slides were tested, three measurements per slide.

### The apparatus

A schematic representation of the apparatus is shown in Figure 1. It comprises the Micro-Force Balance (MFB), where the bubble interactions take place, a complex visual system, and a personal computer, which is used to control the electronic components of the apparatus and to carry out the analysis of the recorded images.

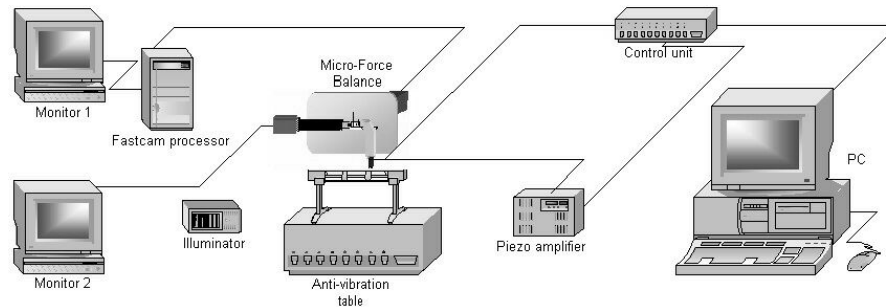


Fig. 1. Schematic representation of the experimental apparatus

The bubble interactions take place in the MFB. In the MFB there is an optical clear glass cell, which is filled with an aquatic solution. The tips of two glass micropipettes are immersed in the aquatic solution, one opposite the other. A bubble is formed at the tip of the lower micropipette by carefully compressing the air inside a flexible tube. The upper micropipette is then moved down to pick up the bubble. A second bubble of the same size is formed similarly at the lower tip. The result of this procedure is the formation of two bubbles, opposite to each other and separated by a liquid film of a few microns. The time needed for this procedure is less than 30 seconds.

The bubbles are forced together by the expansion of a piezoelectric crystal located in a micromanipulator, connected to the lower micropipette. In this way, the lower bubble can move towards the upper bubble and collide with it. An application executed in the computer and written in the VEE Pro programming environment (Agilent Technologies Inc., USA) sends the instructions to a 16-bit multifunction board (Data Translation Inc., MA, USA) to provide the piezoelectric crystal with successive voltages in order to expand it according to the desired rate and expansion. Due to the intrinsic non-linearity of piezoelectric crystals, a Linear Variable Differential Transformer (LVDT) is used to follow the expansion and refer the correct position of its edge with accuracy. The same application in VEE Pro is used for control and data acquisition.

Bubble interactions are monitored and recorded by a high-speed camera, PHOTRON FASTCAM Super 10K (Photron Ltd, San Diego, CA, USA), capable of recording images between 30 and 3000 frames per second (fps). A second CCD camera from Sony Corp. (Tokyo, Japan) is placed at a right angle to the high-speed camera, while both the cameras lay on the horizontal plane. This configuration helps

in the vertical alignment of the bubbles. Each camera is coupled to a single-tube microscope (Edmund Scientific Ltd, York, UK) fitted with a plan achromatic objective lens from Olympus Optical Co, Ltd (Tokyo, Japan). Illumination is provided by a Stocker & Yale Inc. (Salem, USA) M1000 illuminator coupled with a liquid light guide. The high-speed camera fitted with a 10x objective gave an optical resolution of 0.854  $\mu\text{m}/\text{pixel}$ . Recorded images are transferred to the computer for image analysis.

#### **The measurement**

For bubble coalescence experiments in aquatic solutions of HSs or electrolytes, the following procedure takes place. After the formation of the bubbles, their vertical alignment and their positioning to a separation distance of about 10  $\mu\text{m}$ , the piezoelectric crystal is expanded at a rate of 10  $\mu\text{m}/\text{s}$  and the high-speed camera is triggered to record the event. The event ends either with the coalescence of the bubbles, or when the piezoelectric tube has reached its maximum expansion, 100  $\mu\text{m}$ . In the last case, the bubbles have been squeezed but not coalesced. At least 10 repetitions are conducted for each case (bubble size, concentration and type).

It should be noted here that what is being studied is the bubble coalescence behaviour in the froth, not that in the bulk suspension. Since the velocity of the bubbles in the froth is very low, almost static, the conditions used in our experiments are seen as a reasonable approximation to that experienced by bubbles entering from the underside of the froth and then coalescing as they are forced together.

Bubble coalescence in the presence of a solid particle is carried out as follows: The micromanipulator-held bubble (the upper bubble) is transferred to the bottom of the cell, where glass spheres are resting. By aligning the bubble over one sphere, and lowering carefully the micromanipulator, the bubble captures the sphere. In practice, hydrophilic spheres are more difficult to capture, but moderate or highly hydrophobic glass spheres are captured almost immediately. The bubble-particle aggregate is lifted to the proximity of the other micropipette tip. Squeezing further the air inside the lower micropipette, a second bubble is formed. Afterwards, the bubble-particle is moved on top and at the centre of this bubble to a distance of about half the diameter of the sphere. The high-speed camera is triggered to record the interaction, which starts once the piezo starts expanding, forcing the lower bubble to the bubble-particle aggregate. The experiment ends whenever stable agglomerate resulted or bubble coalescence occurred, at which point the camera stops recording.

All the experiments and measurements take place at room temperature, 21-23  $^{\circ}\text{C}$ .

#### **FOAM EXPERIMENTS**

Foams (i.e. structures without particles present) were formed by sparging air at rates increasing from 0.1 to 0.2  $\text{cm}/\text{s}$  into an aqueous solution of 500  $\text{mg}/\text{l}$  polymaleic acid in a vertical 2cm diameter tube. The height of the foam in the column was then measured.

## RESULTS AND DISCUSSION

## EFFECT OF HSs AND ELECTROLYTES ON BUBBLE COALESCENCE

Measurements of the surface tension of aquatic solutions of the HSs used in this work confirmed that the presence of HSs in water lowers its surface tension. The decrease was of the order of 10% of the surface tension of pure water at 23 °C (72.75 mN/m), for solutions of FAs at 100 mg/l. These measurements showed, also, that the surface tension of the aquatic solutions of HSs drops gradually with time, not reaching immediately its final value (see Fig.2). The PMA with MW < 500 Da appeared to drop the surface tension, but less than the two FAs. Electrolytes appeared not to have any great effect on the surface tension of water, increasing marginally its value.

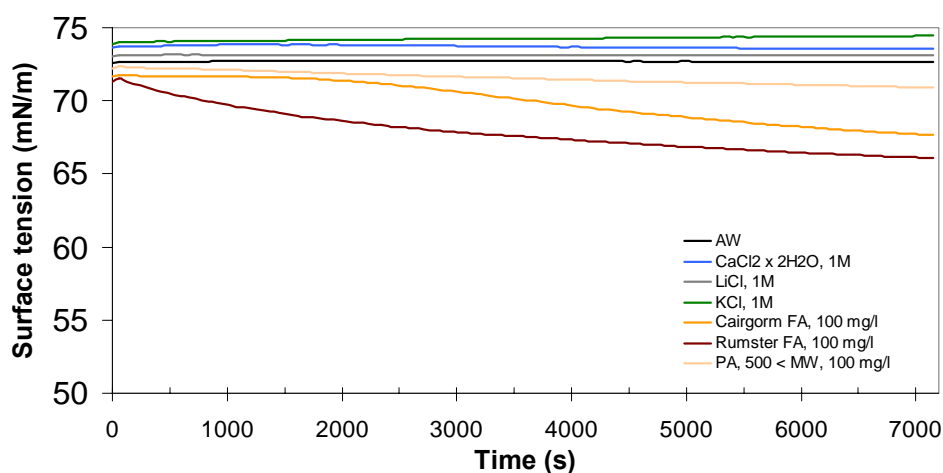


Fig.2. Surface tension of various aquatic solutions at 21-23 °C (pH: 5.0 - 5.5 as the HSs were concerned)

Bubble coalescence experiments were made using pairs of 275- $\mu$ m and 550- $\mu$ m diameter bubbles (about  $\pm$  25- $\mu$ m standard deviation) in water and solutions of electrolytes and HSs. The bubbles were forced to collide at 10  $\mu$ m/s, while their separation was decreasing about 6 nm for every expansion of the piezoelectric crystal. In this work, we used a recording rate of up to 500 fps, so the uncertainty was at least 2 ms; as will be shown below, this uncertainty is not significant, judging by the coalescence times that we measured.

The results for the coalescence frequency for the solutions concerned are shown in Fig. 3. As was expected, there was always bubble coalescence in AnalaR water. There was also 100% coalescence frequency, when the interactions took place in electrolyte solutions, even at high concentration (1M). This was not expected, since published works on the effect of electrolytes on bubble coalescence had shown that electrolytes



could considerably decrease bubble coalescence above a certain concentration (Lessard and Zieminski, 1971). The concentrations were reported to be much less than the concentrations employed in this study. The only explanation that we can give for this discrepancy is the difference in the manner in which the experiments were carried out. In this study, the two bubbles collided coaxially and at low velocity and the liquid film between them was encouraged to thin by the expansion of the piezoelectric crystal, which forced the lower bubble towards the upper. In other studies, the bubbles collided either in bubble columns (e.g. pair of free-to-move bubbles collided at high velocities in a solution) (Deschenes et al., 1998) or in cells, where they had been grown in adjacent nozzles (Lessard and Zieminski, 1971; Oolman T.O. and Blanch, 1986). Double layer repulsions may be more important under such conditions, whereas in our experiments they are overcome by physically pushing the bubbles together.

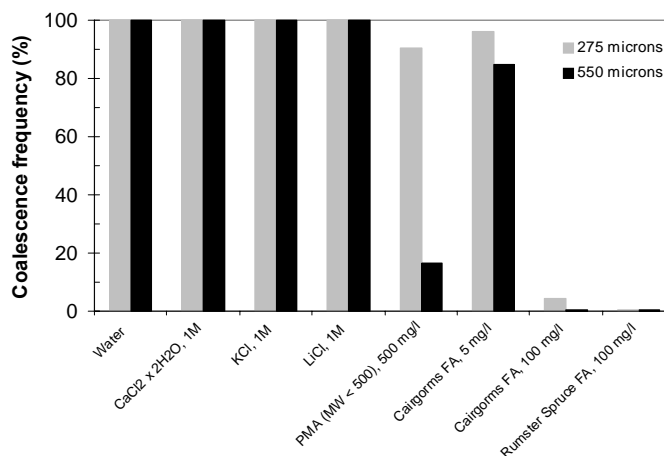


Fig. 3. Coalescence frequencies for bubbles interacting in water and in solutions of electrolytes and HSs

Contrary to the electrolytes, the HSs tested in this work appeared to have a great effect on bubble coalescence. At low concentrations, the coalescence frequency decreased marginally. At higher concentrations, though, the two FAs essentially inhibited the coalescence of bubbles (see). These observations seem to be in accordance with the measurements of the surface tension, where the HSs appeared to be surface active. The inhibition effect of HSs is possibly due to their macromolecules, which raise the steric interaction between colloidal particles (Gregory, 1993).

The coalescence times for the interactions that led to the rupture of the liquid film initially separating the two bubbles are reported in Table 1. Although the values for the case of AnalaR water seem to be much higher than those mentioned in literature

(Oolman T.O. and Blanch, 1986; Tse et al., 1998), this could be due to the use of a different method to collide the bubbles. Indeed, we have conducted bubble coalescence at higher collision rates (30 and 100  $\mu\text{m/s}$ ) and we have found that the coalescence times decreased to just a few ms (data not presented here). Bubbles colliding in electrolytes solution needed about the same time to coalesce as in water. In solutions of HSs, however, the coalescence times were much higher, confirming the great effect of HSs on bubble coalescence.

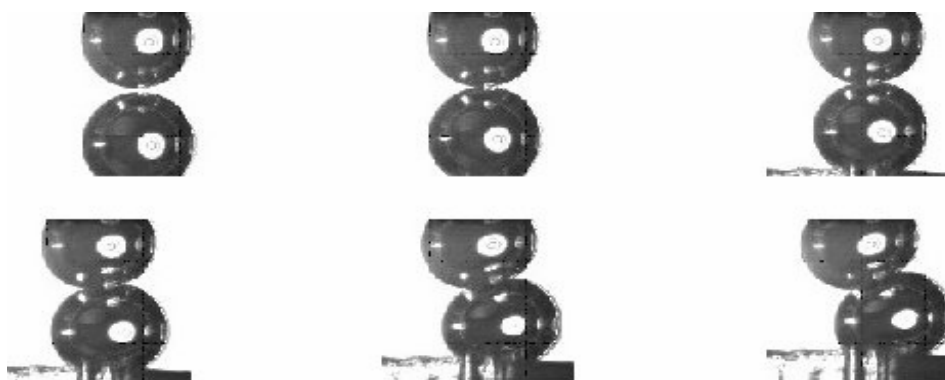


Fig. 4. Two bubbles (275  $\mu\text{m}$  in diameter) are colliding in aquatic solution of FA from Rumster, 100 mg/l, at 10  $\mu\text{m/s}$ . No coalescence. Recording rate: 30 fps. Frame numbers: 0, 60, 120, 180, 240 and 300.

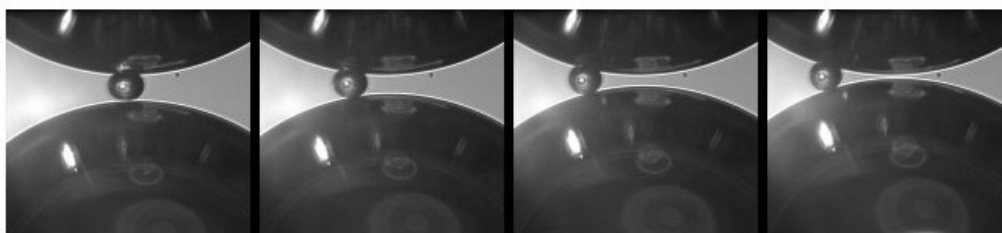
Table 1. Coalescence times of bubbles in water and aquatic solutions of electrolytes and HSs

Liquid	Coalescence time (ms)	
	275- $\mu\text{m}$ bubbles	550- $\mu\text{m}$ bubbles
AnalaR water	66.2	46.6
CaCl <sub>2</sub> ·2H <sub>2</sub> O, 1M	48.5	89
LiCl, 1M	72.4	124.6
KCl, 1M	46.9	114.1
Polymaleic acid (MW < 500 Da), 50 mg/l	90.8	175.5
Polymaleic acid (MW < 500 Da), 100 mg/l	94.8	-
Cairgorms FA, 5 mg/l	595.3	663
Cairgorms FA, 100 mg/l	1400.0	Non-coalescence
FA from Rumster, 100 mg/l	Non-coalescence	Non-coalescence

#### EFFECT OF SOLID PARTICLES ON BUBBLE COALESCENCE

The glass spheres that were tested involved lead glass spheres. Cleaning these spheres just with water resulted in a contact angle of about 30 °C. Thus, these spheres were characterised as moderate hydrophobic. After the silanisation of these spheres, the contact angle of water increase to 105 °C, which means that the surface of the glass spheres was very hydrophobic.

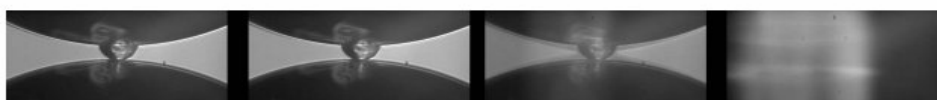
Fig. 5 shows a moderate hydrophobic sphere between two approaching bubbles. Initially, the sphere is hanging from the upper bubble, while the lower bubble is moving upwards. Upon attachment of the sphere with the lower bubble, the sphere did not form a second TPL (e.g. the sphere did not penetrate the lower liquid-air interface), but instead started sliding between the spheres. The bubbles kept approaching each other, as the sphere had no effect on it. The two bubbles coalesced when their apexes touched (image not shown here).



$t_0 = 0 \text{ s}$        $t_1 = 1.17 \text{ s}$        $t_2 = 2.34 \text{ s}$        $t_3 = 3.5 \text{ s}$

Fig.4. A moderate hydrophobic sphere ( $d_{\text{sphere}} = 60 \mu\text{m}$ ,  $\theta = 32^\circ$ ) slides between the approaching bubbles ( $d_{\text{bubble}} = 900 \mu\text{m}$ ): no effect on bubble coalescence. The two bubbles will coalesce (the interaction took place in water) once they will touch each other

However, when the sphere was very hydrophobic, as the sphere shown in the sequence of images in Fig. 5, the situation was different. Almost immediately after the lower bubble came into contact with the sphere, a second TPL was formed. The two TPLs (the first formed between the upper bubble and the sphere, the second between the lower bubble and the sphere) moved to the same line on the surface of the sphere (Fig. 5, image 3). The meeting of the two TPLs resulted to the rupture of the liquid film and the subsequent bubble coalescence (Fig. 5, image 4). The whole interaction took place in less than 6 ms, which shows how a very hydrophobic particle, even of a regular shape, can lead to very fast bubble coalescence.



$t_0 = 0 \text{ ms}$        $t_1 = 2 \text{ ms}$        $t_2 = 4 \text{ ms}$        $t_3 = 6 \text{ ms}$

Fig. 5. A very hydrophobic sphere ( $d_{\text{sphere}} = 78 \mu\text{m}$ ,  $\theta = 105^\circ$ ) forms immediately a 2nd three-phase contact line (TPC) upon attachment with the lower bubble ( $d_{\text{bubble}} = 1000 \mu\text{m}$ ). The two TPLs meet at the same line on the bead (image 3) and the liquid film that initially separated the bubbles ruptures.

The interaction took place in water

It has to be noted at this point that the interactions took place in pure water. It remains to be seen what the effect is of particles, both moderately and highly hydrophobic, on bubble coalescence in other aquatic environments, especially those containing surfactants, such as HSs.

#### DETERMINING $P_f$

The coalescence frequencies described above were used to calculate  $P_f$ . Since the film formed between the two bubbles was essentially flat and the overall bubble deformation small, the exerted pressure is inversely proportional to the radii of the bubbles being forced together. Figure 7 shows  $P_f$  as a function of the pressure exerted (each point is the average of many experiments).

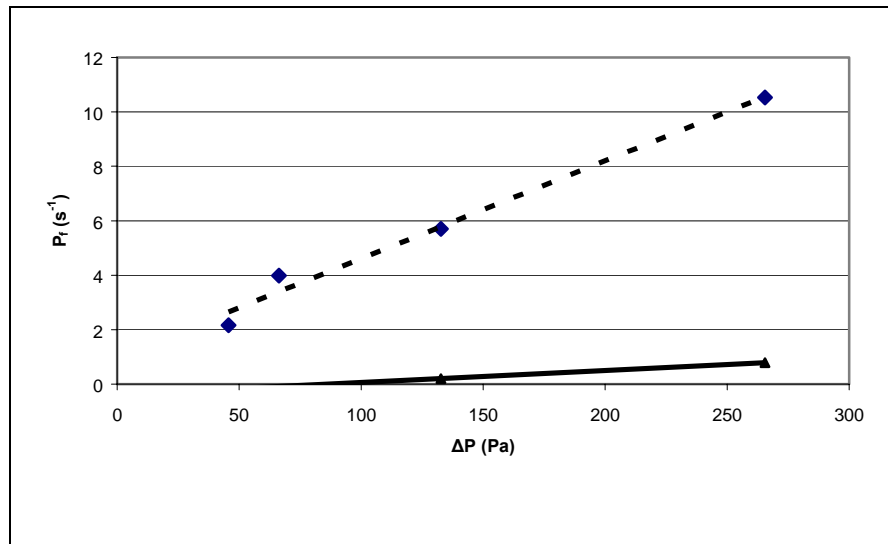


Fig. 7:  $P_f$  vs pressure exerted from micro-manipulation experiments (----- PA 50 mg/l, — PA 500 mg/l)

Figure 7 clearly shows that the relationship between  $P_f$  and the applied pressure is linear, as would be expected from film drainage theory (equation 1). The intercept is approximately zero for the low concentration experiments, which indicates virtually no electric double layer barrier, while the higher concentration experiments suggest at least some pressure barrier to coalescence.

#### FOAM EXPERIMENTS AND SIMULATIONS

The high film failure frequencies shown in Figure 7 indicate that, even for the higher concentration, polymaleic acid foams will be very unstable. The foam height results are plotted with results from the simulations in Figure 8. For both the experimental and simulated results a near-linear relationship between foam depth and air rate is observed.

Note that the simulations suggest a strong dependency between the incoming bubble size and the equilibrium foam depth, with larger bubbles producing deeper foams. This foam is very unstable, with only a few layers of bubbles existing. Unfortunately, in these experiments, the accurate measurement of the incoming bubble size was not possible, but the incoming bubble size was in the range of 1.5mm to 2.5mm, which, as shown in Figure 8, gives close correspondence between experiment and theory.

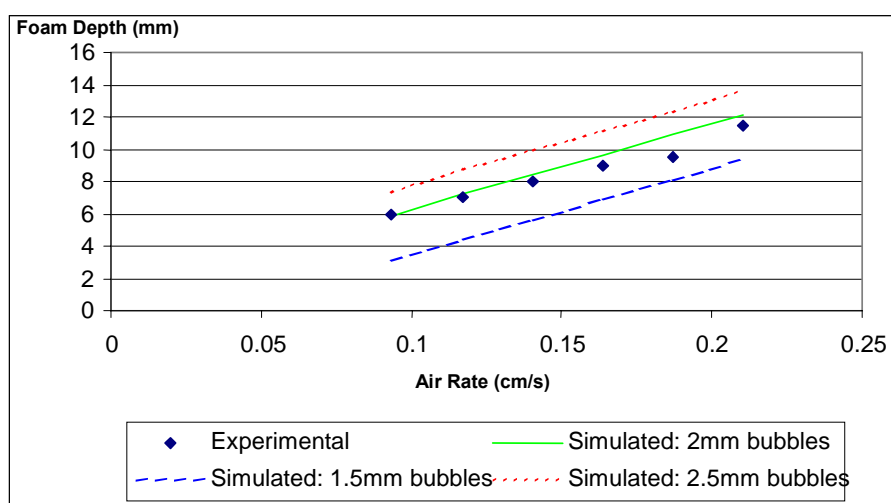


Fig. 8: Experimental and simulated results for 500 mg/l polymaleic acid solution

## CONCLUSIONS

Humic substances can have an effect on bubble coalescence, and as a consequence on froth stability. Humic substances at low concentrations will retard bubble coalescence, while at high concentrations can prevent coalescence completely, due to the steric interaction brought about by the macromolecules of humic substances. On the other hand, the electrolytes appear not to have any considerable impact on bubble coalescence under the experimental conditions used (i.e. at low velocity collisions). The presence of humic substances in natural water may partly interpret the stability of froths in DAF tanks in water-treatment plants. If not all the humic substance has been coagulated before entering the DAF tank, it will contribute to the stability of froth, along with other impurities also present in natural water.

By direct observation and recording of the behaviour of glass spheres between two bubbles in pure water, the following conclusions can be drawn:

- Spheres of moderate hydrophobicity ( $\theta \sim 30^\circ$ ) could not form a TPL with the second bubble. When they were pushed against it, they slid along the surface of the bubble.

- As long as the low hydrophobic spheres were between the two bubbles, no film rupture occurred and the bubbles remained intact. When the spheres eventually slipped completely from the space between the bubbles, the bubbles then came in contact and, depending on the purity of the liquid film, immediately coalesced.
- Highly hydrophobic glass spheres ( $\theta > 100^\circ$ ) penetrate the lower bubble, forming a second TPL. The bubbles coalesced because the two TPLs moved on the same position over the surface of the sphere.

The form for the drainage time limited case of  $P_f$  was experimentally verified and simulations of the height of foam columns using this form showed close correspondence to experimental results. Further investigation on the effect of solid particles on bubble coalescence is needed, particularly testing their effect when the interaction takes place in aquatic solutions of surfactants, and not just in water, as the case in this study.

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**Spyridopoulos M., Simons S., Neethling S., Cilliers J.**, *Wpływ substancji humusowych i cząstek ciała stałego na koalescencję pęcherzyków powietrza i stabilność piany w odniesieniu do zdyspergowanego powietrza w procesie flotacji*, Physicochemical Problems of Mineral Processing, 38, (2004) 37-52 (w jęz. ang.).

W pracy przeprowadzono badania nad wpływem substancji humusowych (naturalne surfaktanty), elektrolitów i cząstek ciała stałego na koalescencję pęcherzyków powietrza, a w konsekwencji na stabilność piany. Nowa aparatura została wykorzystana do pomiarów sił oddziaływań między dwoma pęcherzykami o jednakowym kształcie. Oddziaływania zostały zarejestrowane przez specjalną kamerę. Obrazy z kamery pozwoliły określić częstotliwość i czas koalescencji, jak również mechanizmy oddziaływania. Dwa rodzaje substancji humusowych użyto do badań oraz trzy rodzaje elektrolitów. Okazało się, że substancje humusowe miały istotny wpływ na koalescencję pęcherzyków. Wpływ elektrolitów był minimalny. Kule szklane o średnim i wysokim stopniu hydrofobowości powierzchni były umieszczane między pęcherzykami. Kule o dużej hydrofobowości powierzchni powodowały szybszą koalescencję pęcherzyków, podczas gdy, kule o średniej hydrofobowości powierzchni nie wykazywały tego efektu. W pracy przedstawiono dane dotyczące częstotliwości koalescencji. Te dane zostały użyte do weryfikacji parametru  $P_f$ , określanego jako częstotliwość rozerwania filmu. Parametr ten został użyty w modelu symulacyjnym, który określał wysokość piany w naczyniu. Otrzymane wartości parametru  $P_f$  na podstawie modelu, zostały eksperymentalnie zweryfikowane.