

CHALMERS



The influence of surfactant chemistry on flotation deinking

Master of Science Thesis in the Master Degree Programme, Material and Nanotechnology

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Abstract

This master thesis addresses the influence of surfactants on deinking flotation. The deinking system was studied without the fatty acid emulsion in the pulping stage instead being replaced by a non-ionic surfactant. A number of commercial non-ionic surfactants were chosen to give a broad spectrum of basic parameters such as CMC, cloud point, HLB molecular weight and chemical structure, and then evaluated in order to get indications of which of the parameters that are of importance for the process. The experiments were conducted at different concentrations, and the results were correlated with the critical micelle concentration (CMC) curve.

The non-ionic surfactants that showed the best results in the initial screening process were chosen for further investigations. The variation of the non-ionic surfactant concentration in the flotation showed that a concentration above 50 g of non-ionic surfactant per ton of dry fibre gave no improvements. Experiments with a concentration of 10 g of non-ionic surfactant per ton of dry fibre gave poor results. A suitable dosage seems to be 30-50 g of non-ionic surfactant per ton of dry fibre.

Use of a non-ionic surfactant instead of a fatty acid emulsion in the flotation gave a higher amount of wet reject but a lower level of dry content in the reject, indicating an overall improved yield and possible economical benefits.

The overall influence of the physico-chemical parameters of the non-ionic surfactant on the flotation efficiency was not so clear from this study, since many of the investigated surfactants performed well. However, the results indicate that an ethylene oxide/propylene oxide block copolymer structure and a molecular weight of several thousand g/mol were beneficial.

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1. Background

Paper is a widely used material, and has many applications from packaging to printing material. As the use of paper increased radically in the 1970's, the demand for a cheap source of raw material grew, and the recycling of paper increased.

In Europe, the main technique for recycling paper is deinking flotation. Flotation is a process to selectively separate the hydrophobic ink particles from the hydrophilic fibres.

For a good result of the flotation there are three main sub processes that needs optimisation,

- The detachment of ink particles from the fibre,
- The adhesion of the ink particle onto the bubbles and
- The removal of froth and ink particles from the flotation cell¹.

These three processes are greatly affected by the use of different chemicals in the process. In Europe, the main surface-active agents used in flotation are a fatty acid emulsion (often containing ethylene-propylene oxide based non-ionic surfactants) as a detacher and disperser of the ink, together with a fatty acid. The fatty acid is saponified under the alkaline conditions to form calcium soap, acting as a collector and foam controller.

There is an interest from the industry to introduce a more efficient and less expensive raw material to replace the fatty acid in the process. An interesting alternative to the fatty acid emulsion as a dispersing agent is commercial surfactants. The focus of research studies on this subject has been on non-ionic surfactants mainly, since an- and cationic surfactants doesn't promote detachment of ink and can lead to substantial fibre losses during flotation.

There is however a lack of research in the area of flotation deinking enhanced with non-ionic surfactants regarding the influence of basic parameters, such as CMC (critical micelle concentration)² and cloud point³ of commercial surfactants in flotation. This diploma work is indented to give insight into if these parameters could be used for recommendations of surfactants for use in flotation.

2. Theory

2.1. Full-scale recycling of paper

2.1.1. Waste paper as a raw material

The recycling of paper, took off in the 1970's when the use of paper increased sharply and the need for cheaper raw material was increased. In Sweden in 2008, 83% of all paper was recycled. Collected paper is divided into different categories of mixed office waste (MOW), old magazines (OMG), old newsprint (ONP), paperboard and corrugated fibreboard. The composition differs greatly between applications, but the key components are fibre (70-90%), filler material (5-30%) and additions like strength agents, whitening agents and inks. OMG and ONP are the main source of paper in flotation deinking mills. OMG is characterised by a high amount of filler and may be coated and are often printed with rotogravure inks. ONP often has a high amount of mechanical pulp and low amount of fillers. The print is often of the offset type⁴.

2.1.2. Printing inks

Ink consists of pigments or dye, a binder to attach the ink to the paper and other components such as for example solvents and additives. The pigment, such as carbon black and titanium dioxide, give colour to the paper. The ink used to print ONP and OMG often has a binder of natural oil. The composition of inks used for offset printing (most common for e.g. newsprint) and rotogravure printing (common for e.g. magazines) may differ. For example, offset inks have a higher viscosity,

while rotogravure inks are less viscous. Most inks are hydrophobic, which is a prerequisite for the deinking chemistry to work. Thus, water-based inks used in flexographic printing are very difficult to remove, and paper or board printed with flexo has to be recycled separately.

2.1.3 Aging of ink

During the aging of the printed paper the ink reacts in a multi step polymerisation process to form cross linkage between hydrocarbon chains. This leads to improved cohesiveness of the ink particles as well as bond strength between the particles and the substrate.⁵⁶

The steps of the polymerisation are described by Castro et al to be involving initiation, propagation and termination of free radicals.

The timeframe for this procedure is in the scale of 4-6 months⁷ for mineral oil inks but occurs much more rapid in vegetable oil inks according to Castro.

The aging can be slowed down by the addition of oxidation inhibitors for some time.

2.1.3. The industrial flotation deinking process

The flotation deinking in the mill begins with the pulping of paper and magazine in a drum pulper, with the addition of chemicals, the ink is released from the fibre. The mix is then screened to remove staples, plastics and other debris. The pulp is then set to react in a reactor or swelling tower and after that sent to the flotation cell. In a flotation process, many flotation cells are used in serial. After the flotation step, the paper is bleached to give a satisfactory level and sent to a storage tower.

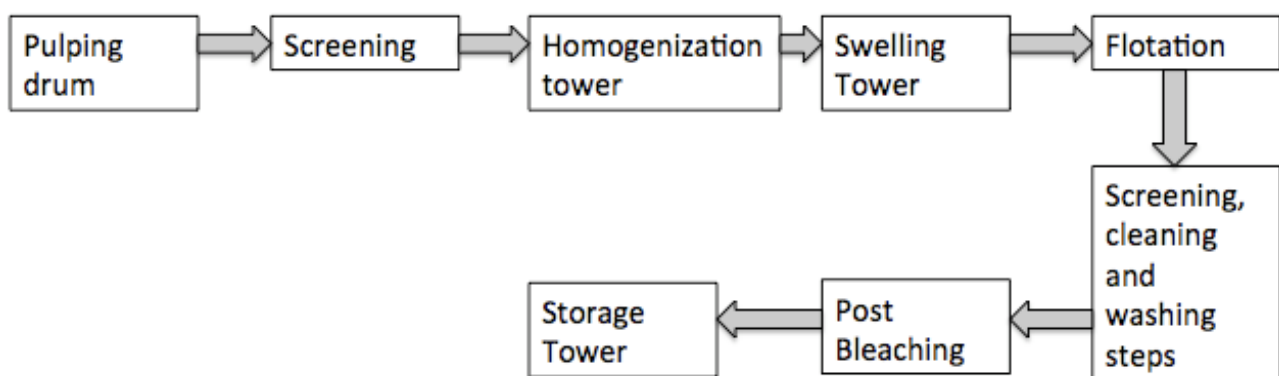


Figure 1. Flow sheet of deinking mill

2.2 Optical properties of paper

The quality of a flotation deinked paper is judged by its optical properties. Two parameters are often used; brightness and effective residual ink concentration. These are used to create a benchmark of measurement, on processed paper.

2.2.1 Brightness

The brightness of a paper is defined as the reflectivity blue light of the effective wavelength 457nm with a distribution from 400-500nm. The reflection is measured on a scale from 0 - 100% ISO.

Notable is that this measurement only takes into account the blue region, ignoring the yellow and red portions of the spectrum and that the brightness measuring method was developed to monitor the bleaching process of paper.

2.2.2 Effective Residual Ink Concentration (ERIC)

The brightness is not an effective way to monitor the deinking process. Comparisons of recycled newsprint and virgin newsprint gives the same reflectance in brightness but in the infrared region the two can vary greatly. The residual ink has a known relationship to reflectance in this region⁸.

The infrared region is chosen for measurement because of the reason of that this region is only affected by ink, not from dye, lignin or other colorants.

When the infrared coefficient of the residual ink is known, an Effective Residual Ink Concentration can be calculated⁹.

$$ERIC = \left(\frac{k_{sheet}}{k_{ink}} \right) \times 10^6$$

Where the *absorption coefficient* (k) of ink, k_{ink} , has shown an absorption of $10,000 \text{ m}^2/\text{kg}$. The k_{sheet} of the sample at 950 nm may be calculated by:

$$k = s \left[\frac{(1 - R_{\infty})^2}{2R_{\infty}} \right]$$

The *scattering coefficient* (s) of the sample at 950 nm may be calculated by:

$$s \left[\frac{1000}{(w(1/R_{\infty} - R_0))} \right] \ln \left[\frac{(1 - R_0 R_{\infty})}{(1 - R_0/R_{\infty})} \right]$$

Where $w = \text{grammage} (\text{kg}/\text{m}^2)$ and where R_0 and R_{∞} are the reflectance of the sample backed with the black cavity and the reflectance backed with a stack of samples and are expressed in decimals.

The ERIC is expressed as points per million (ppm).



Figure 2. Low ERIC



Figure 3. High ERIC

The ERIC value is a value of the effect of the remaining ink and not an actual measure of remaining ink. As the figures show above, there is a difference in the ERIC between agglomerated ink and evenly distributed ink on the sample. The sample with the agglomerated ink particles will appear whiter (low ERIC) than the one with distributed ink (high ERIC).

2.3 Deinking chemistry

The purpose of the deinking process is to separate a system of hydrophobic material (ink) from hydrophilic material (fibre) by using the differences in their chemical properties.

The chemistry of the system needs to be formulated so that the surfaces of the ink particles are highly hydrophobic-unstable surfaces. This gives ink agglomeration and strong adhesion to air bubbles for the flotation process, according to Beneventi et al¹⁰.

The flotation deinking is based on three steps; the first being the preparation of a pulp suspension from a mixture of news- and magazine paper by the addition of chemicals and water. Sodium hydroxide is added to give an increased and faster release of ink from the fibre. Further, hydrogen peroxide, surface-active agents and sodium silicate are added to the pulp. Their function in the

process will be described below. A process temperature of 40-60°C¹¹ and a concentration of around 10-15% dry content of pulp are kept during pulping.

The second step is the agglomeration of ink particles in the pulp to create aggregates in the size range between 10-100µm. According to Johansson, the size of the agglomerates is more important for effective flotation than their hydrophobicity¹². In the pulping stage, the surface-active agents are added to act as collectors and dispersants for the released ink particles to form these aggregates.

The third step is the adhesion of the agglomerated ink particles on the air bubbles, and thereby the separation of the ink and fibre in the flotation cell. The suspension is diluted with water to a dry content of about 0,8-1,5%. The bubbles are formed in the bottom of the cell, and as they rise toward the top the agglomerates, if of adequate size, attach on the air bubbles' surfaces. On the top of the flotation cell a layer of foam is formed from the risen bubbles. The foam containing the agglomerated ink particles can then be removed while the fibres remain in the cell.

The chemicals used in the deinking process to create a favourable system in the pulp and their function will be described more thoroughly below.

2.3.1 Sodium hydroxide

Sodium hydroxide (NaOH or lye) is used to adjust the pH towards the alkaline region of pH 9-10. The swelling of the fibre caused by the lye can help the mechanical release of the stiffer ink from the surface of the fibre. The alkaline environment also saponifies the fatty acids and hydrolyses the ink resins¹³. The NaOH causes an ionisation of the carboxylic groups of the cellulose fibres and saponification of some ink binder and acid resins in the wood¹⁴. The release of the ink is due to ionisation of fibres and the ink's surface groups, generation of electrostatic repulsive forces, mechanical stress at the ink/fibre interface after swelling and release of fatty acid soaps².

2.3.2 Hydrogen peroxide

The main reason the hydrogen peroxide (H₂O₂) is added to the process is to prevent the yellowing of the paper that occurs with the addition of sodium hydroxide. The hydrogen peroxide forms a perhydroxyl anion (HOO⁻) in water which attacks the groups causing yellowing in the lignin called chromophores. The hydrogen peroxide can also break the chemical cross-linkage that is formed between alkyl binders of the ink when stored and dried¹⁵.

2.3.3 Sodium silicate

The reason for the addition of sodium silicate is to stabilise the hydrogen peroxide. By inactivating the metal ions in the process causing breakdown of hydrogen peroxide, and by maintaining a stable pH an optimisation of the effect of the hydrogen peroxide is acquired¹⁶. There are also other minor effects of the sodium silicate such as improved dispersion of ink, due to attachment to colloidal particles.

2.3.4 Fatty acid

Fatty acid mixtures are commonly used in flotation as dispersants and (in their saponified form) as collectors. These mixtures are often of commercial grade and primarily contain C 14-18 carbon chains, which consists mainly of stearic, oleic, palmitic and linoleic acids. The blends are sensitive to change in properties, directly influencing foaming, selectivity, and carry over of chemicals to the paper machine¹⁷. In an alkaline water environment the fatty acids react with the sodium hydroxide to form a soluble salts. This saponification gives rise to an anionic surfactant RCOO⁻ and a sodium counter ion. The process is often rich in calcium ions, added separately or from the paper. These ions substitute the sodium ions forming calcium salt. The calcium salt forms highly hydrophobic soap flakes which act as agglomerators of the detached ink particles.

The amount of fatty acids transferred from the deinking plant to the paper machine is about 20% but can vary from 0 to 100% depending on the plant and process conditions¹⁸. This can cause problems in the papermaking performance, resulting in weaker strength and changed wetting characteristics. The fatty acid soap can be added to the process in the pulping stage to act as collector and/or in the

flotation step to get a better control of the foaming properties. Shorter chain fatty acids enhance the foaming ability but ink removal is reduced.

2.3.5 Non-ionic surfactants

Non-ionic surfactants are used today in flotation mainly as dispersion agents. There are many surfactants that have been produced especially for the flotation deinking process and are used in the concentration range of 0,001-0,01 % on dry fibre. The surfactants used in flotation deinking are non-ionic due to their low sensitivity towards the hardness of the water. Ionic surfactants do not improve the result of the flotation and can lead to high yield losses in the flotation stage². Non-ionic surfactants are also preferred when working at neutral flotation deinking conditions where the use of calcium soaps is difficult because of the low alkalinity. The dispersion of surfactants is caused by the adsorption of the hydrophobic ink particles, thereby creating a hydrophilic surface and thereby increasing detachment of ink.

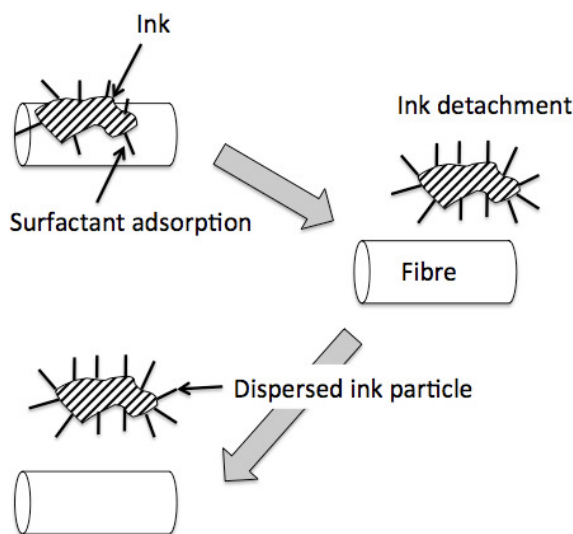


Figure 4. Non-ionic surfactant dispersion of ink.

The non-ionic surfactants used in deinking often, to some part, consist of ethylene oxide (EO) and propylene oxide (PO) polymers. According to Theander and Pugh¹⁷, many patents point to that the optimal performance of the surfactant is with a hydrocarbon chain length of 16-18. The EO:PO ratio should be between 1:2 and 4:1¹⁷. These types of non-ionic surfactants are often produced as a block co-polymer, but there are indications in patents¹⁹ that random co-polymers are more effective giving higher flotation efficiency of newsprint.

Chemical name	Chemical structure
Ethylated fatty alcohol	$R - O - (CH_2 - CH_2 - O)_n - H$
Ethylated fatty acid	$O = R - C - O - (CH_2 - CH_2 - O)_n - H$
Propylene Oxide/Ethylene Oxide Block copolymers	$HO(CH_2CH_2O)_x(CH(CH_2O)_y(CH_2CHO)_z)H$

Table 1. Some of the surfactants used in deinking chemistry today

The hydrophilic-lipophilic balance (HLB) of a non-ionic surfactant affects the flotation efficiency to some extent. HLB values describe how the surfactant interacts with water soluble and water repellent substances. In deinking flotation it has been suggested that non-ionic surfactants with an HLB value of 14-15 are optimal for deinking of paper and magazine mixtures²⁰. HLB values are

theoretical values and are calculated from the chemical groups that the non-ionic surfactants are made up from.

The HLB number is not an unambiguous indication when looking at the behaviour of non-ionic surfactants. The HLB value does not account for the temperature sensitivity of a non-ionic surfactant, that for example makes non-ionic the surfactant give an o/w emulsion at room temperature and w/o emulsion at elevated temperatures²¹.

This phenomenon is called the cloud point and is an important factor for non-ionic surfactant and therefore affects the choice of surfactants in the process. The EO/PO surfactants become soluble in water due to hydration of the ether oxygen's group in the polyoxyether group. Increases in temperature break this bond between the water and ether oxygen group, thus resulting in a decrease in water solubility of the non-ionic surfactant in the water. The system phase separates into two phases and due to this a turbid appearance is observed, giving the name cloud point²².

Deinking efficiency has been generally correlated with the cloud point. The highest deinked sheet brightness obtained when the process temperature was within 5°C of the surfactant cloud point³.

There are a number of positive and negative aspects of using non-ionic surfactants in the process, according to Johansson²³, where some of which are listed in table below.

Positive aspect	Negative aspect
Reduced ink redeposition	Increased ink fragmentation (dispersion)
Decreased air bubble coalescence	Reduced ink agglomeration
Reduced fibre losses	Reduced collection of ink by air bubbles
Increased foaming in the flotation cell	Increased foaming in the flotation cell

Table 2. Positive and negative aspects of non-ionic surfactants in the process.

2.4 Surface chemistry of deinking

The deinking process contains many different surface phenomena, where many are not still fully understood. Here, these will be addressed and, to the extent possible, be explained

2.4.1 Surface chemistry of the flotation

The flotation process contains many steps and due to its complexity there are many different proposed mechanisms of the working of these. This has led to many different models for the mechanism and presumed steps.

- In the Schweizer mechanism soap adsorbs on the ink surface, lowering the surface energy. After detaching; ink particles are collected by air bubbles. The mechanism is not taking the Ca^{2+} effect on soap into account nor the surfactant adsorption on bubbles.
- The Bechstein mechanism focuses on precipitated soap being the collector of suspended ink particles and floated by air bubbles.
- The Ortner mechanism is similar to Bechstein mechanism, but the mechanism is divided into three steps; soap adsorption to ink particles, the generation of a system constituted by ink particles and air bubbles and calcium ions acting as bridge between ink and bubbles.
- The Hornfeck mechanism takes into account the negative electrical charge of the ink surface on the soap adsorption. Soap is not adsorbed by its hydrophobic part but they precipitated on the ink particle causing the ink particles to become hydrophobic. The hydrophobic ink particles are then floated by air bubbles.
- The most widely accepted is the Larsson-mechanism, due to it being the most complete, proposed by Larsson²⁴. The mechanism is based on five phenomena occurring in the process: the parameters of the ζ -potential, the concentration of Ca^{2+} ions, the precipitation of soaps and the agglomeration of ink particles. These are considered to be the main parameters affecting the process. The five steps the mechanism is built around are:

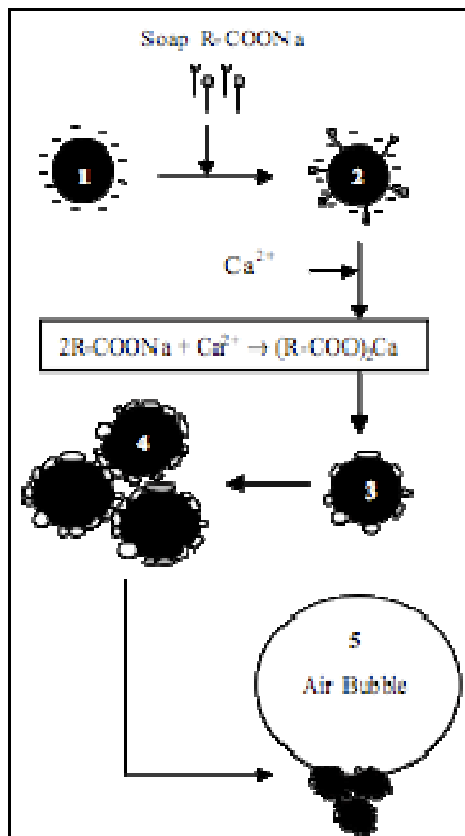


Figure 6. The Larsson mechanism

1. An alkali ionises the fatty acids $R - COO^-$ at the ink surface providing a stabilisation for the suspended ink particles.
2. The adsorption of surface-active agents at the surface of the ink particle is driving the dispersive interaction between the ink and surfactant.
3. Addition of Ca^{2+} ions increases the negative zeta potential of the dispersed particles and causes formation of calcium soap particles on the surface, making the particles even more hydrophobic.
4. The repulsive forces and the increase in surface energy cause ink particles to agglomerate.
5. The hydrophobic particles are easily floated, due to their increased size.

2.4.1 Effect of temperature

The temperature of the flotation deinking process is, as mentioned above, 40-60°C. Changes on this factor has only a small effect on a calcium soap systems, due to the effect on many other parameters and Johansson²⁵ claims that the temperature dependence of calcium soap collectors are nearly non-existent, due to the low solubility of calcium soaps even at high temperatures. In a system where the main surface-active agent is a non-ionic surfactant there is a larger focus on the temperature parameter due to the large impact the temperature has on the non-ionic surfactants properties. Little has been published on the temperature dependence of such a system though there are a few notable indications.

The optimal detergency of a non-ionic surfactant for newspaper prints, according to Borchardt²⁶, is around the cloud point temperature of the non-ionic surfactant.

Johansson claims that a temperature above the cloud point is needed in flotation for destabilising the dispersed ink particles to hinder them from forming to small agglomerates.

2.4.2 Influence of pH

An elevated alkalinity can increase the efficiency of the flotation process as proposed by Forster²⁷. The increased efficiency was explained by the increase of zeta potential, from a potential of -25mV at pH 6 to -50mV at pH 10. This was explained by the increase in electrostatic repulsion of charged fibre and ink particles. A higher pH also gives faster and more efficient ink agglomeration but the contact angle of the ink is decreased²⁸. It has been shown that the contact angle is not the crucial parameter, but rather the size and the surface characteristics of the ink are decisive for the outcome of the efficiency of the flotation¹⁷.

The flotation process is often carried out at a pH of 8-10 where an optimal balance between sufficient alkalinity for good saponification and minimum formation of chromophores exists.

2.4.3 Influence of the hardness of the process water

The concentration of Ca^{2+} in the process water is a critical parameter when calcium soap is used as a collector. It has been shown that out of the many factors the process depend upon, the Ca^{2+} concentration is a prime factor contributing to yield losses. A lower value of Ca^{2+} usually gives lower stock losses, according to Theander et al.¹⁷. High Ca^{2+} concentrations can give many negative effects on the process such as scaling and deposits on paper machine during processing.

An optimal concentration level of Ca^{2+} and a slight excess of free fatty acid give optimal flotation results for calcium soap flotation²⁴. If these levels are altered, ink aggregates can, as a result, become smaller than their optimal size and flotation efficiency reduced. Also, an increase in fatty acid levels, due to low calcium levels can give lower precipitation of calcium soaps. This may in affect the foaming properties of the system, causing the efficiency to drop and carryover of chemicals to later stages in the process to increase.

Experiments by Schwinger and Dobias²⁹ further show the increase in fibre losses due to high calcium concentrations by the use of oleate as a collector and the by addition of non-ionic surfactant. However, by doubling the concentration of non-ionic surfactant the stock loss was found to be reduced. The mechanism of this is still unclear. The optimal concentration of calcium ions is around $2,7 \times 10^{-3}$ M according to Theander et al¹⁷.

The fact that the system is very sensitive to variations of the calcium concentration leaves room for much improvement. A deinking system built around a non-ionic surfactant could perhaps be the answer. Non-ionic surfactants are insensitive to calcium ions and give benefits such as good foaming properties if properly chosen.

2.4.4 Concentration of non-ionic surfactant

The concentration of the non-ionic surfactant used in the flotation process directly affects many parameters in the process. Some of the parameters affected are the size of the agglomerated ink, the size of the air bubbles and the foaming properties.

The concentration of the non-ionic surfactant is tied to the critical micellisation concentration (CMC) where the non-ionic surfactants does not lower the surface tension but starts to form micelles in the solution.³⁰

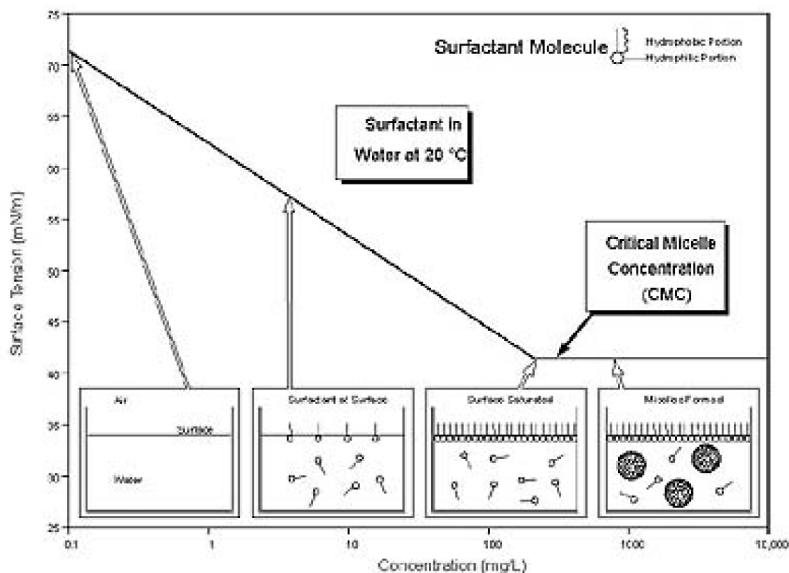


Figure 7. The characteristics of a CMC graph.

The CMC curve is characterized by two stages. The first stage is the lowering of surface tension by accumulation of surfactants at the interfaces until all the interfaces are covered by surfactant. At the CMC concentration the surface tension is not further lowered with increased concentration, and the formation of micelles from the free monomers in the solution starts (second stage).

For non-ionic surfactants, an elevated temperature decreases the CMC. As for pH, in the CMC increased the pH range of 7-12. Other surfactants, mainly ionic, lower the CMC of non-ionic surfactants.³¹ The main roles for surfactants in today's flotation deinking are as dispersion agents and froth controllers. At temperatures below the cloud point and at high concentrations of the non-ionic surfactant, the size of the agglomerates is affected towards smaller agglomerates according to Johansson¹⁵. The calcium soap and the ink particles are stabilised at a small size by the non-ionic surfactant, so agglomeration is hindered.

Beneventi reports similar findings with different concentrations when using non-ionic surfactants in flotation; that in spite of the reduction in bubble size, the surfactant repressed the flotation of particles. The increase in the surface area flux was not sufficient to counteract the drop in bubble surface tension and in the pulp/ink contact angle³².

The use of non-ionic surfactant at small concentrations seems most favourable and an increase in concentration, gives no further benefits.

Johansson¹⁵ does report that when increasing the temperature, thus using the non-ionic surfactant above the cloud point, the non-ionic surfactant starts to aggregate at all concentrations with an optimum at 10^{-4} M. This behaviour occurs probably because of the increased hydrophobicity of the non-ionic surfactant above the cloud point.

3. Experimental

3.1. Materials

The non-ionic surfactants used in the experiments were all of technical grade. The main properties of the non-ionic surfactants are shown in table 3. The non-ionic surfactants were all dissolved in water at 1g surfactant / 100g tap water and dispersed by heating.

Surfactant	Chemical Structure	Molecular weight (g/mol)	CMC (g/l)	Cloud Point (°C)	Surface tension (mN/m)	HLB Value
Surfactant 1	Glycerol based ethylene	Ca 4000	x	44	35	x

	oxide propylene oxide co-polymer					
Surfactant 2	ethylene oxide/propylene oxide block polymer	1400	x	30-36	39	x
Surfactant 3	Alcohol Polyglycol Ether	Ca 6000	x	46-52	36	x
Surfactant 4	Non-ionic polymeric surfactant based on C16-18 alcohol + ethoxylate/propoxylate	Ca 5000	x	70	45	12,3
Surfactant 5	Alcohol(C13) Ethoxylates(10EO)	x	0.10	65-73	28	13,5
Surfactant 6	Alcohol(C12-16) Ethoxylates propoxylate (EPO)	x	0.024	39-43	31	11,5
Surfactant 7	EO-PO-block polymer	2650	x	50	41	x
Surfactant 8	PO-EO-block polymer	2450	x	33	41	4
Surfactant 9	C13-15 Oxalcohol	520	4.6E-4M	43	28	12
Surfactant 10	Non-ionic fatty polyether	x	x	43,5	x	x

Table 3. Non-ionic surfactants used in experiments. X= information missing. The molecular weight of surfactant 10 is likely to be in the range of surfactant 4 since they are both designed for industrial deinking purposes where a higher molecular weight traditionally is preferred.

The chemicals used in the pulping stage of the process was

Chemical	Origin
Sodium Hydroxide(NaOH)	Base chemical on the lab, 45% concentration
Silicate	BI3340, a technical silicate, 39-41% dry content
Hydrogen peroxide(H ₂ O ₂)	Diluted (10%) 30%, reagent grade, Scharlau.
Water(H ₂ O)	Tap water at a temperature of 50-60°C

Table 4. Pulping chemicals origin

The decomposition of hydrogen peroxide over time requires a daily concentration determination, in order to decide the concentration. The approach for how this was done is shown in appendix II.

The ONP used in all the experiments was GT and its sports supplement, from the 10 June 2010 and the OMG was Svensk dam tidning, the may issue of 2010.

Filter paper for suction filtration was Macherey-Nagel, MN617. Fluka analytical provided the polyethyleneimine solution used in sample preparation

The process water, white water, used in the CMC measurements was taken from Hylte bruk 101005.

3.2. Methods

3.2.1 Flotation equipment

The method for investigation used in this study was flotation of pulped paper in a Voith Labor Flotaion Cell Delta25. The cell is constructed from the principles of a flotation step in a full-scale deinking mill. It is designed to be user friendly and to give small variations between users to give high reproducibility. The cell, shown in the picture bellow, is built around a 25dm³ open tank, with an aeration rotor placed in the bottom. The baffle plate controls the water flow in the tank and on the top there is an automatic foam remover to remove excess foam down into the foam outlet. The

operator switch has three settings, standby mode with circulation, air injection and injection through the pipe (any medium). The airflow is shown below the operators switch and was kept constant, 7-8, during the flotation. During flotation a 0,5 dm³ bottle was used to splash water on the walls of the cell to keep the ink from sticking to the walls.

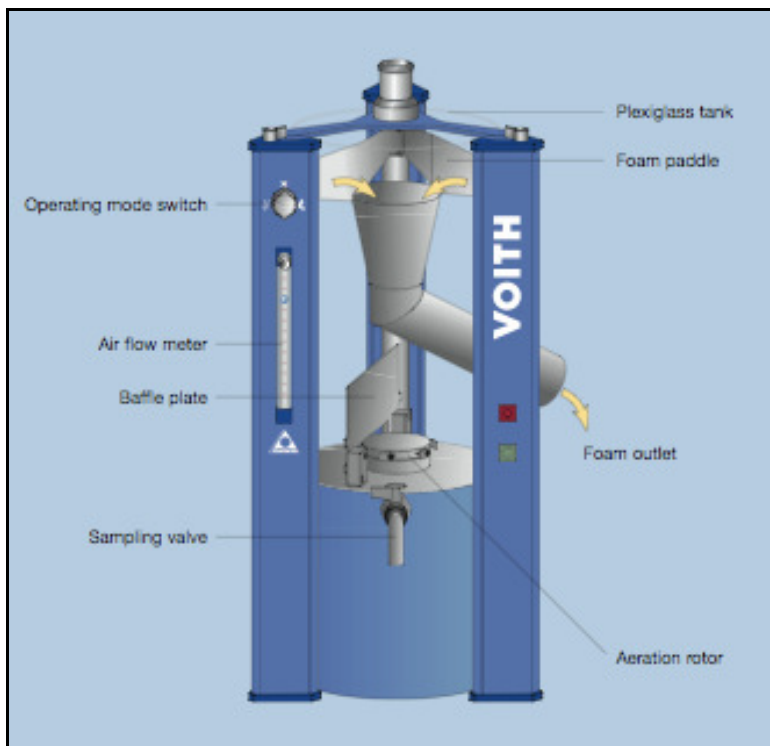


Figure 8. Voith Labor Flotation Cell Delta25³³

3.2. Deinking experiments

The method used for the experiments was based on that of the process of a deinking plant flow sheet. This was to ensure that the results in the study could be as similar to a deinking plant as possible but on a more manageable scale.

The shredding in a plant is done by tearing the paper rather than cutting it, due to fibre damage in cutting. The paper was shredded into approximately 4 to 6 cm² after the staples and loose advertising was removed from the old newspaper (ONP) and old magazines (OMG).

A paper-mix of 70% ONP and 30% OMG was used. The pulp was prepared according to the recipe according to appendix 0. The mixing in a Kitchen Aid, for 20 minutes, was done to distribute the chemicals evenly. The addition of hot tap water was added and the pulp was placed in an oven to give the chemicals reaction time and fibre time to swell. The temperature was 53-55°C and the time was 30 minutes. After evenly dividing the pulp and further addition of water, dispersion of the pulp was carried out in a resolver for 3 minutes. The shear forces serve to disrupt larger aggregates and thereby establish an average particle size within a particular system¹. After dispersion the pulp was added into the flotation cell.

An addition of soap, accord, to the dispersed pulp was done before addition of an additional hot tap water in the range of 50-60°C to a 1% pulp consistency. Samples were collected before and after the flotation.

Part of the samples of the flotated and the unflotated pulp sample was washed in a hyperwash with approximately 20 litres of fresh water to remove resolved ink particles.

The flotated and unflotated pulp, both hyperwashed and unwashed, was filtered by suction to form fibre cakes. The samples were then flattened and dried before analysis. The yield of the flotation was measured from the foam outlet of the flotation cell. Both wet and dry yield was measured during the experiments.

3.3 Brightness and effective residual ink concentration (ERIC) measurement equipment

The brightness and ERIC value of the samples was obtained by measurements on a spectrophotometer, a Color Touch 2 from Technidyne.

3.3.1 Basic Principle

Spectrophotometry is the study of electromagnetic spectra that emits from visible or near visible light. The spectrophotometer involves a photometer, for measuring light intensity as a function of the light source wavelength. The measured is the adsorption of light emitted. The set up for a spectrophotometer is shown in the picture below, with the main steps being a □

1. The light source shines on the sample.
2. Reflections are filtered through a monochromator to screen away unwanted wavelengths.
3. A photocell in a photo detector measures the adsorbed light.

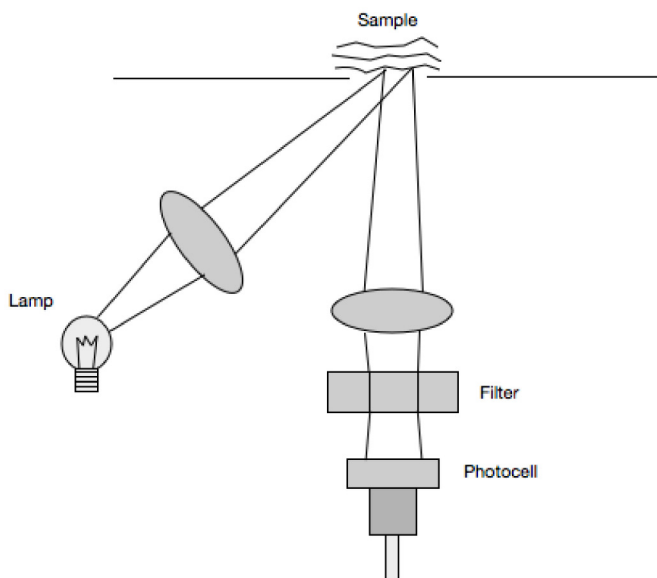


Figure 9. Basic principle of spectrophotometer

3.4 Critical micellisation concentration measurement equipment

The Du Noüy ring measurement method was used to determine the effects of the process conditions on CMC of the surfactants. The apparatus used in the experiments was Sigma 70 system unit and for dosage of the surfactant a Metrohm 765 Dosimat 10ml was used.

3.4.1 Basic Principle

The platinum ring is one of the oldest ways of measuring the surface tension. The basic principle around the measurement is raising the liquid until it comes in contact with the ring; the liquid is then lowered again so that the liquid surface is stretched. The film is stretched until a maximum force (F_{max}) is experienced, being the recorded measurement. The maximum force is parallel to the direction of motion, giving at this exact moment a contact angle of 0° .

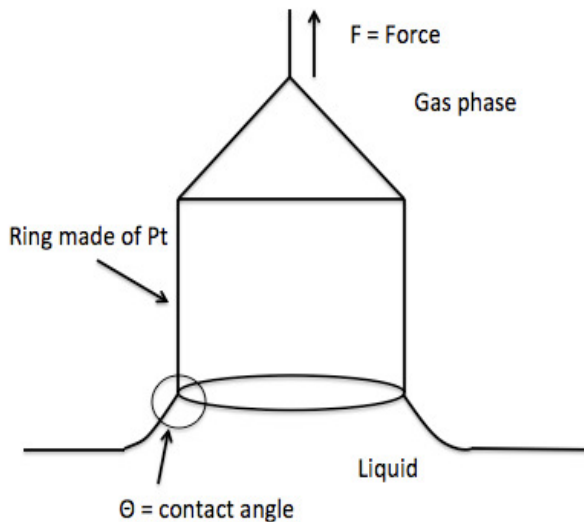


Figure 10. The ring setup.

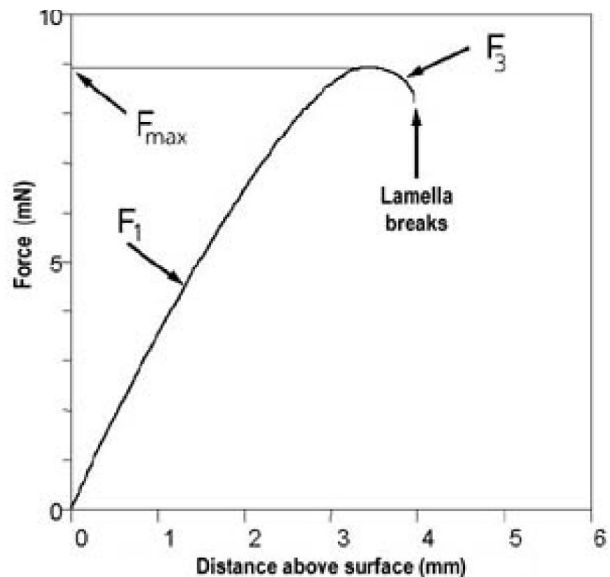


Figure 11. The force measurement

3.4.2 CMC measurement

The surface tension measurements were used to create a CMC curve. The surface tension was measured at increasing concentrations and the results showed at what concentration level the CMC were.

The measurements were conducted according to appendix V; a stock solution of non-ionic surfactant and milliQ/process water was prepared at a concentration of the theoretical CMC value of the non-ionic surfactant. Following that the stock solution was rinsed through the automatic pipette used for addition of stock solution to the measurement equipment.

The surface tension was measured at the chosen concentration span and recorded to form a CMC curve.

The temperature was varied and experiments were performed at 23, 30, 40 and 50°C in milliQ/process water.

4. Results and discussion

4.1. Screening of different surfactants

In the first part of the study, various non-ionic surfactants were screened. The emulsion from the reference recipe was replaced by a non-ionic surfactant. The initial dose of non-ionic surfactant was 30 g/ton of paper and was obtained from industrial standards.

Some of the non-ionic surfactants used in screening were specifically designed for flotation deinking i.e. Surfactant 4 (a non-ionic polymeric EO/PO surfactant with a molecular weight of approx. 5000) and Surfactant 10 (a non-ionic polyether), and some were standard commercial surfactants designed for different uses. The non-ionic surfactants were chosen to provide a broad spectrum of what is recommended in the literature but also non-ionic surfactants that would not, according to the literature, be optimal for flotation deinking. The non-ionic surfactants in this screening were similar to the extent of their chemical structure, but displayed a wide range of different basic parameters such as molecular weight, CMC, cloud point and HLB-value (See table 3).

During the flotation, it was observed that the amount of ink in the froth decreased with time, usually between 3-4 minutes. It was also observed that the amount of fibre increased in the froth during this time. This was later seen as a trend in all flotations conducted.

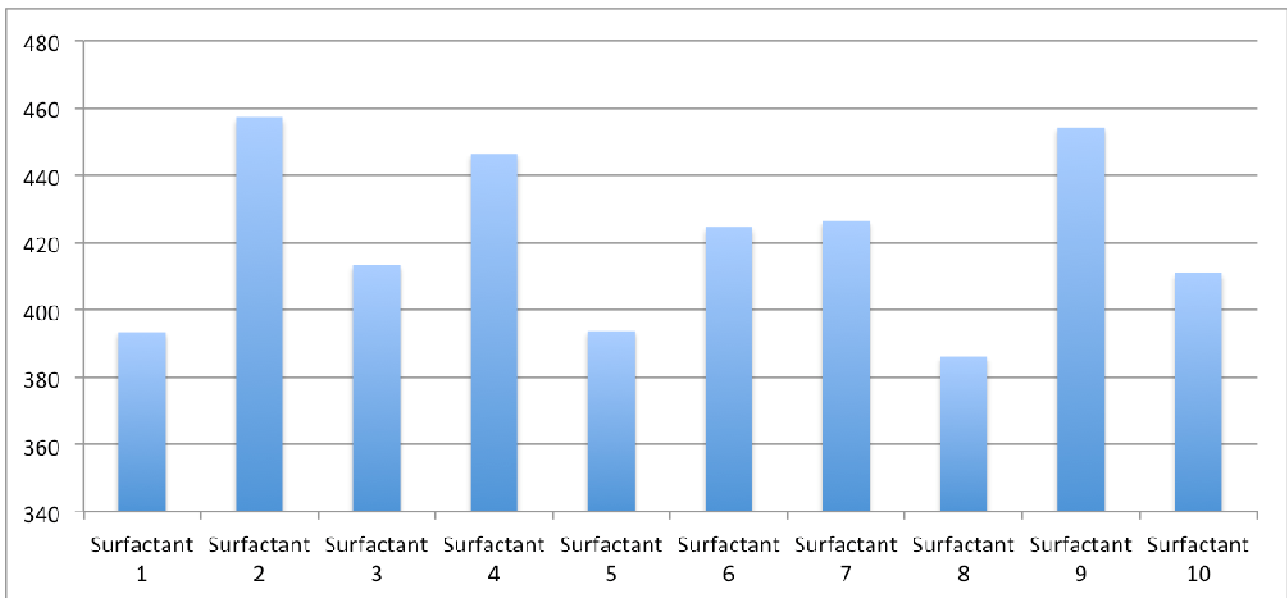


Figure 12. The ERIC value of flotated pulp.

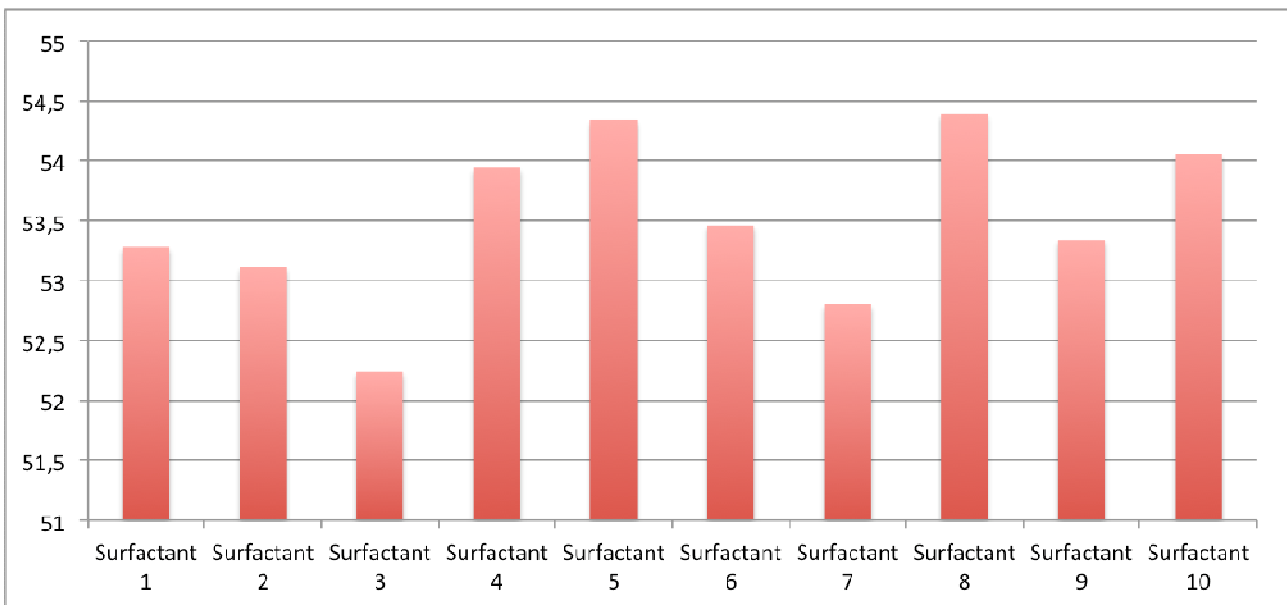


Figure 13. The Brightness value of flotated pulp.

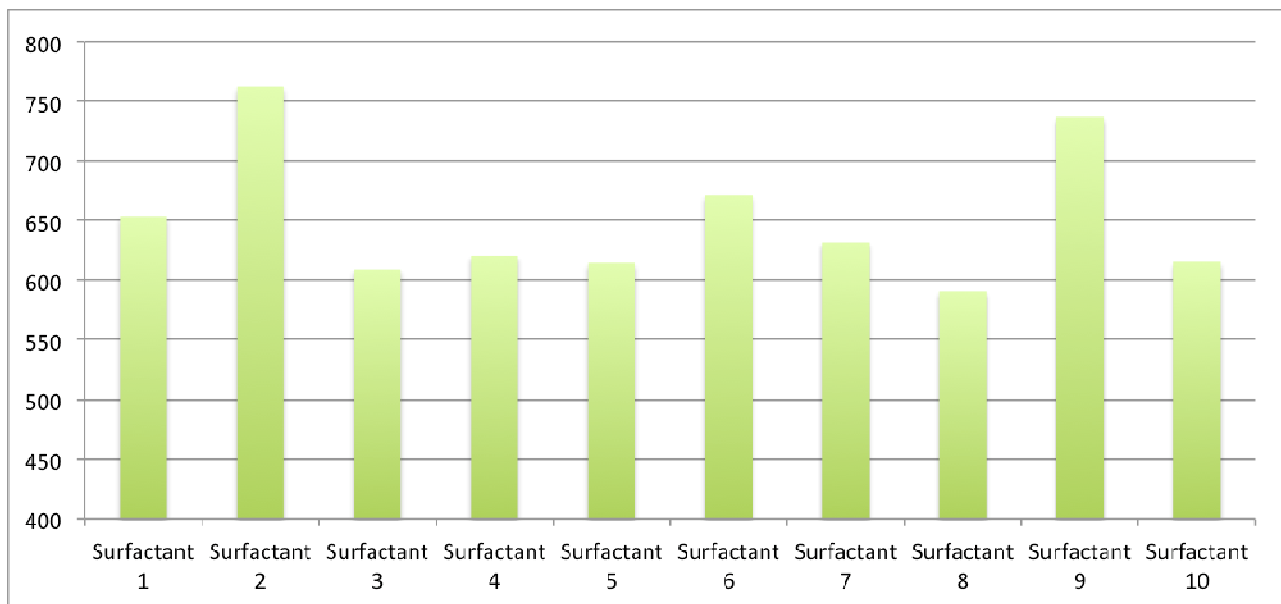


Figure 14. Amount of Reject(g)

Surfactant	Flotated ERIC	Flotated Brightness	Flotated HW* ERIC	Flotated HW* Brightness	Unflotated ERIC	Unflotated Brightness	Unflotated HW* ERIC	Unflotated HW* Brightness
Surfactant 1	393,5	53,28	126	57,67	1092,5	43,28	135,4	57,85
Surfactant 2	457,2	53,11	171,7	56,57	1361	40,68	186,7	56,37
Surfactant 3	413,4	52,24	139,3	56,35	1077,1	43,26	150	57,03
Surfactant 4	446,5	53,94	155,1	56,99	1204,7	41,49	173,1	56,89
Surfactant 5	393,8	54,34	137,6	57,24	1154,7	41,4	143,3	57,24
Surfactant 6	424,6	53,46	153,1	56,34	1195,2	42,41	168	56,65
Surfactant 7	426,5	52,8	158,6	55,47	1119,5	42,98	169,5	56,44
Surfactant 8	386,2	54,39	147,3	56,34	1138	41,17	163,2	56,51
Surfactant 9	454,3	53,34	151,5	57,2	1226,5	41,36	157,1	58,06
Surfactant 10	411,1	54,05	163,1	56,89	1165,8	42,11	151,2	56,17

Table 5. All optical results of the screening. *)Hyperwashed

Surfactant	Δ ERIC	Δ Brightness	Reject (g)
Surfactant 1	699	10	653,7
Surfactant 2	903,8	12,43	762
Surfactant 3	663,7	8,98	609,3
Surfactant 4	758,2	12,45	620,7
Surfactant 5	760,9	12,94	614,5
Surfactant 6	770,6	11,05	671,3
Surfactant 7	693	8,82	631,9
Surfactant 8	751,8	13,22	590,9
Surfactant 9	772,2	11,98	736,8
Surfactant 10	754,7	11,94	615,4

Table 6. Delta values, reject and yield loss.

As the results show the ten flotations provides a relatively narrow range of results. Neither the ERIC nor the brightness values show any clear direction in which surfactant that would work best in our environment under the actual conditions.

There is however certain things that stands out. The non-ionic surfactants with a rather small molecular weight (surfactant 2, MW=1400 and surfactant 9, MW=520) show a tendency to give a

higher ERIC value. They also increase the amount of reject from the flotation cell that decreases the yield of the process.

The value of unflotated ERIC can be used to give an indication of the agglomeration of the ink particles in the pulp before flotation. As can be seen the value for the two smallest non-ionic surfactants are at the top of the ERIC values for unflotated pulp, suggesting redeposition of the ink onto the fibre. The dispersing effect of the small non-ionic surfactants counteracts with the agglomerating effect of the soap precipitates, thereby decreasing the effect of the flotation.

The brightness' of the ten flotations shows values of between 52,24 – 54,39. The brightness values do however not correspond to any clear correlation. It is however important to note that such a difference in the Brightness is not a negligible factor.

4.2. Concentration effects

The concentration of a non-ionic surfactant is important to the process in many ways. There have been links between concentration levels and for example size of air bubbles in the system¹⁷, the size of the precipitated soap particles³⁴ and the surface tension of the stock. All these are parameters that influence the process.

In the next step of the study, the concentration levels were correlated to the CMC curve. The CMC curve can give good indications of how the non-ionic surfactant works in the system, from the lowering of the surface tension to the formation of surfactant micelles at higher concentrations.

The non-ionic surfactants used in this part of the study, were chosen to give a broad spectrum of parameters; low and high molecular weight, low and high cloud point and varying HLB value. Since the CMC of some of the most promising non-ionic surfactants at the process temperature (50° C) were not provided, CMC measurements were made. The results of the CMC measurements are shown in Table 7 and the complete curves in Appendix VI.

Surfactant	CMC (g/l) from own measurements(MilliQ water)
Surfactant 4	0,0036
Surfactant 9	0,0018
Surfactant 10	0,0059
Surfactant 8	0,0233

Table 7. CMC of non-ionic surfactants

First, three levels of concentration were tested with the surfactant 4, where the maximum concentration value was the measured CMC concentration and the lowest was half of the measured CMC concentration level (see figure 15). This was then used as a guideline to make the selection of concentrations for the other non-ionic surfactants.

Equilibrium Surface tension versus Concentration

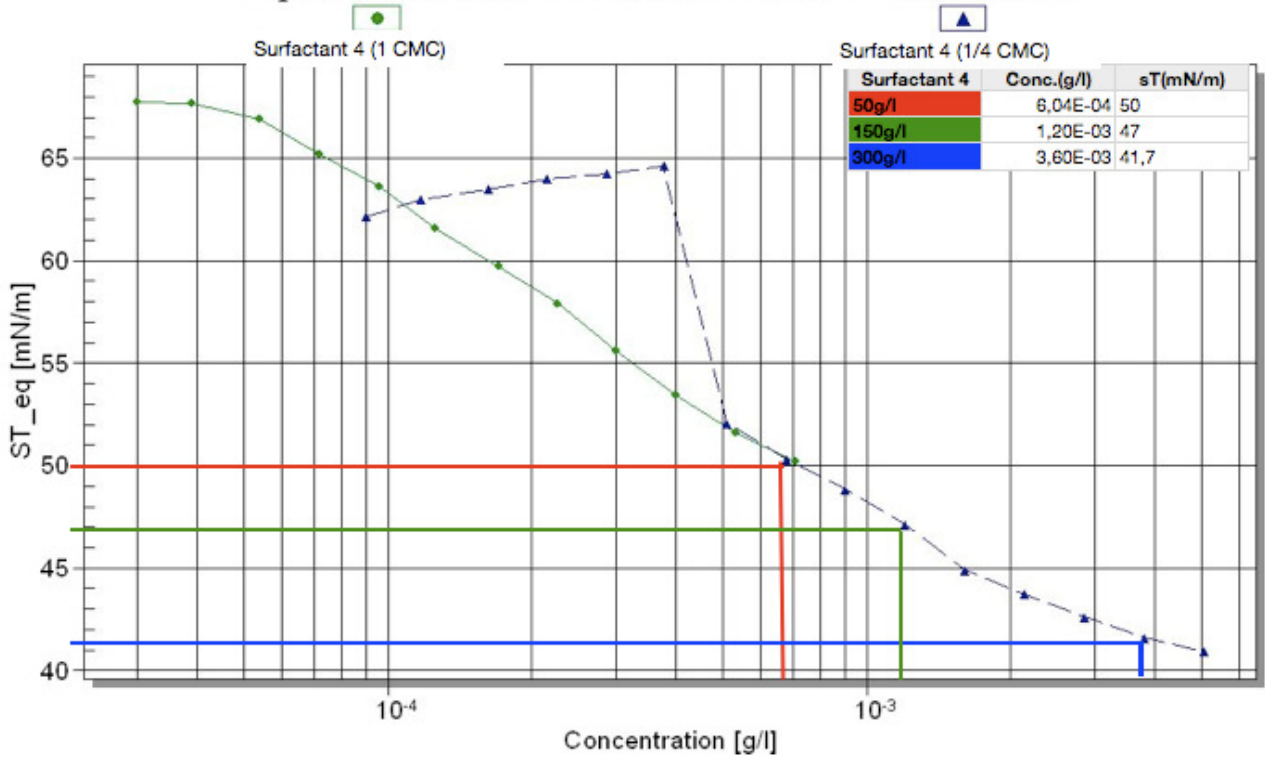


Figure 15. Selection of concentration levels of Surfactant 4 according to the CMC curve.

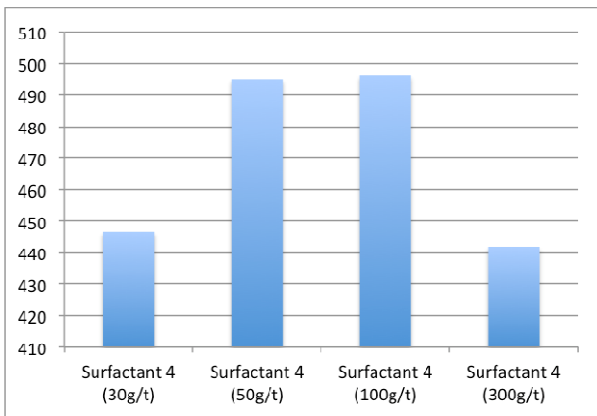


Figure 16. Flotated ERIC

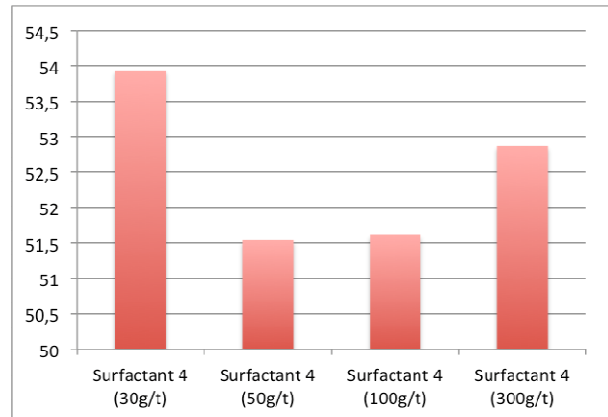


Figure 17. Flotated Brightness

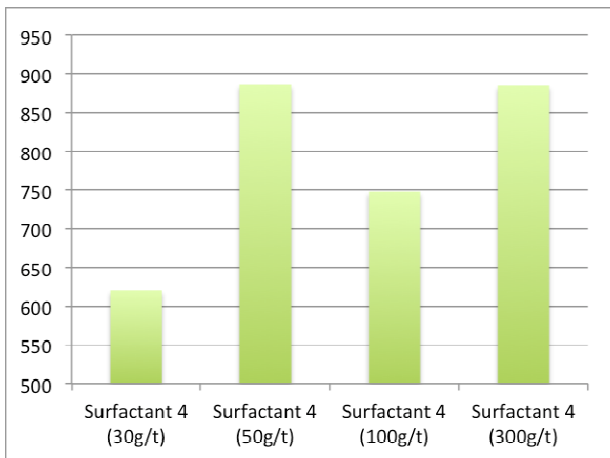


Figure 18. Reject(g)

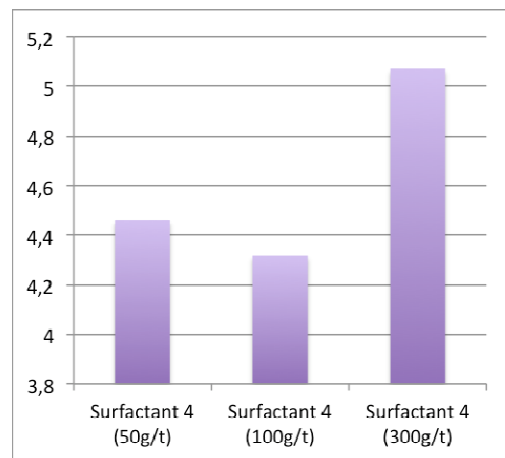


Figure 19. Yield (%) losses

Surfactant concentration	Flotate d ERIC	Flotated Brightness	Flotated HW ERIC	Flotated HW Brightness	Unflotated ERIC	Unflotated Brightness	Unflotated HW ERIC	Unflotated HW Brightness
30g/ton	446,5	53,94	155,1	56,99	1204,7	41,49	173,1	56,89
50g/ton	495	51,54	221,4	53,9	1257,6	40,49	227,2	55
100g/ton	496,2	51,61	202,2	55,34	1185,8	43,04	215,4	55,55
300g/ton	441,8	52,87	204,6	55,36	1324	41,25	214,5	55,64

Table 8. All optical properties of optimal concentration flotation

Surfactant concentration	Δ ERIC	Δ Brightness	Reject (g)	Yield loss (%)
30g/ton	758,2	12,45	620,7	X
50g/ton	762,6	11,05	886,4	4,4
100g/ton	689,6	8,57	748,2	4,3
300g/ton	882,2	11,62	885,3	5,1

Table 9. Delta values, reject and yield loss.

The ERIC values show no decrease with increased surfactant concentration until the concentration reaches 300g/ton. The same is displayed for the brightness values, which doesn't increase until a 300g/ton. The high concentration does, however, cause other problems like a fairly large amount of reject and an increased yield loss.

The hyperwashed flotated ERIC values show that the best ink detaching effect is obtained at the lowest concentration, i.e. 30 g/ton. However, this experiment was performed with fresher paper than the higher surfactant concentration, meaning that the ink could have been more easily detached.

The highest concentration on the CMC curve at 300 g/t was excluded from the rest of the experiments. The increase in addition to this level gives no additional advantages to that of 30 g/ton, thereby it is not justified. Also, the increased level of surfactant in the deinking process due to recirculation of process water in the mill would give this high level of addition further negative effects in practice.

Experiments were then conducted with a concentration level that should give the same surface tension, 50mN/m, for all the non-ionic four surfactants chosen for further study. These levels were read from the CMC curves measured previously for all the non-ionic surfactants. This approach would possibly give us an indication of the influence of the effect of other parameters (cloud point, HLB), when keeping the same surface tension in the flotations.

Surfactant	Concentration (g/L) at 50mN/m	Concentration in g/ton
Surfactant 4	6,04E-04	50
Surfactant 8	2,44E-04	20,15
Surfactant 9	1,10E-03	91,07
Surfactant 10	1,30E-03	107

Table 10. Concentrations at 50mN/m

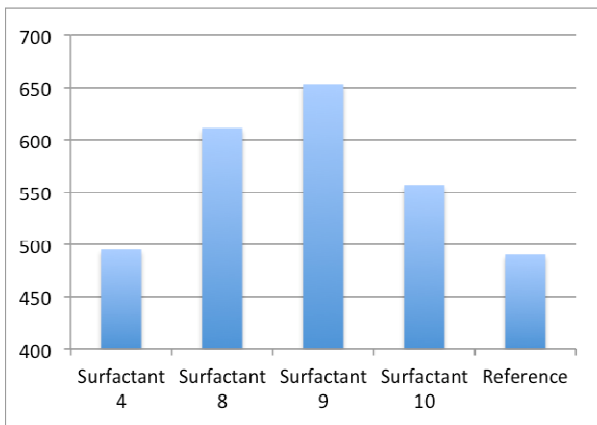


Figure 20. Flotated ERIC

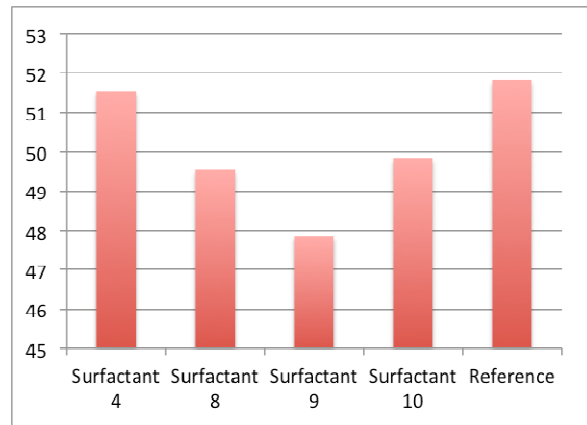


Figure 21. Flotated Brightness

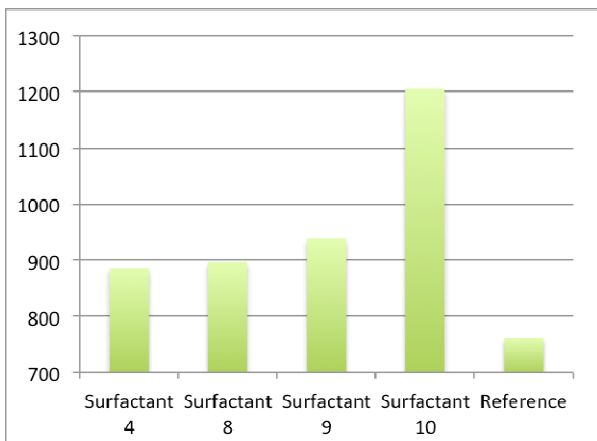


Figure 22. Reject(g)

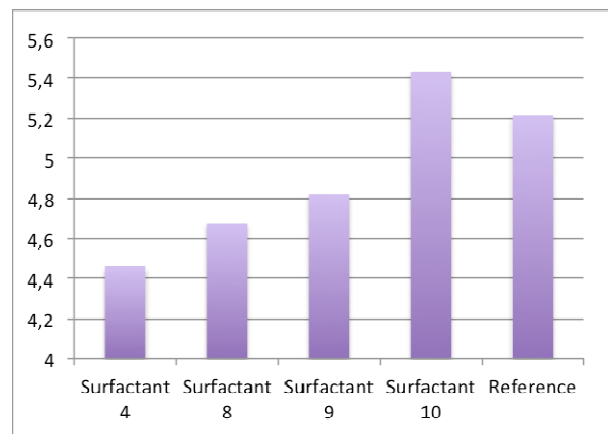


Figure 23. Yield loss(%)

Surfactant	Flotated ERIC	Flotated Brightness	Flotated HW ERIC	Flotated HW Brightness	Unflotated ERIC	Unflotated Brightness	Unflotated HW ERIC	Unflotated HW Brightness
Surfactant 4	495	51,54	221,4	53,9	1257,6	40,49	227,2	55
Surfactant 8	611	49,53	237,1	54,03	1360,4	39,72	255,4	53,86
Surfactant 9	653	47,86	234,7	53,98	1433,8	36,9	244,8	54,13
Surfactant 10	556,9	49,84	236,1	53,44	1307,3	40,56	253,7	53,52
Reference	490,2	51,83	261	53,95	1278,9	41,64	292,3	53,6

Table 11. All optical properties of CMC curve flotations

Surfactant	Δ ERIC	Δ Brightness	Reject (g)	Yield loss (%)
Surfactant 4	762,6	11,05	886,4	4,46
Surfactant 8	749,4	9,81	896,4	4,67
Surfactant 9	780,8	10,96	937,9	4,82
Surfactant 10	750,4	9,31	1204,90	5,43
Reference	788,7	10,19	761,6	5,21

Table 12. Delta values, reject and yield loss.

The results show that Surfactant 4 gives similar result to that of a reference experiment using a fatty acid emulsion instead of a non-ionic surfactant. These are also the best results. The small non-ionic surfactant, Surfactant 9 (a C₁₃₋₁₅ oxoalcohol), shows weak results with high ERIC value and low brightness as in the initial trials. Surfactant 8 (a PO/EO block copolymer) gives the second best result with low values on the reject and a fairly high yield.

Surfactant 9	653	47,86	234,7	53,98	1433,8	36,9	244,8	54,13
Surfactant 10	556,9	49,84	236,1	53,44	1307,3	40,53	253,7	53,52
Surfactant 8	555,6	49,9	237,2	53,26	1212,6	40,42	247,2	53,2
Surfactant 4	496,2	51,61	202,2	55,34	1185,8	43,04	215,1	55,55
Reference	490,2	51,83	261	53,95	1278,9	41,64	292,3	53,6

Table 13. All optical properties of 100g/ton concentration flotation

Surfactant	Δ ERIC	Δ Brightness	Reject (g)	Yield loss (%)
Surfactant 9	780,8	10,96	937,9	4,82
Surfactant 10	750,4	9,31	1 204,9	5,43
Surfactant 8	657	9,48	864,4	5,17
Surfactant 4	689,6	8,57	748,2	4,31
Reference	788,7	10,19	761,6	5,21

Table 14. Delta values, reject and yield loss.

The results show that this level of concentration gives a small decrease in ERIC value for the PO/EO copolymer, Surfactant 8, but gives a higher loss of fibre from the cell. The only non-ionic surfactant that can compare with the reference flotation using no non-ionic surfactant is still Surfactant 4. But the increased concentration does not give any positive effect on the flotation; however, an increased loss in the fibre can be noted for all non-ionic surfactants.

The general trend for the trials was that an increased level of concentration gives little to no improvement of the flotation results. The initial trials with a level of 30 g/ton gave the strongest results.

4.3. Sodium hydroxide concentration adjustment

The amount of sodium hydroxide (NaOH) was, due to a miscalculation, too high in all of the previous experiments. The added amount of NaOH was 8,89kg/ton of paper where the correct addition would be 4kg/ton.

The pH difference between the trials has been calculated from the definition of pH and pOH:

$$pOH = -\log_{10} \frac{[OH^-]}{mol \times dm^3}$$

$$pH + pOH = 14$$

The complete calculations are displayed in appendix VIII.

Addition of NaOH	pH in pulping stage	pH in flotation stage
2,45g	12,57	11,42
1,125g	12,24	11,08

Table 15. The different pH levels in the experiments

This affects the results of previous experiments and to see how much reference test were performed. These were made with Surfactant 4, Surfactant 8 and Surfactant 10, since when these had been the most promising surfactants. It was also tested how low of an amount of surfactant could be added while maintaining effect, by adding 10g/ton of non-ionic surfactant.

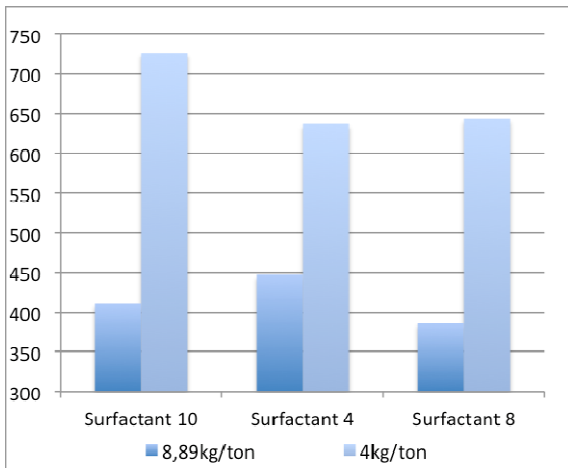


Figure 28. ERIC values non-ionic surfactant addition 30g/ton

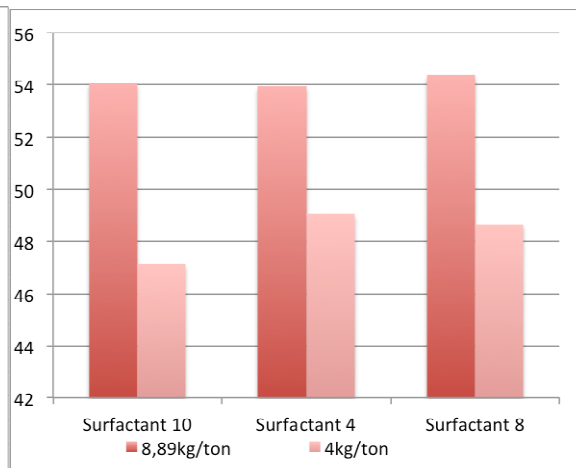


Figure 29. Brightness values non-ionic surfactant addition 30g/ton

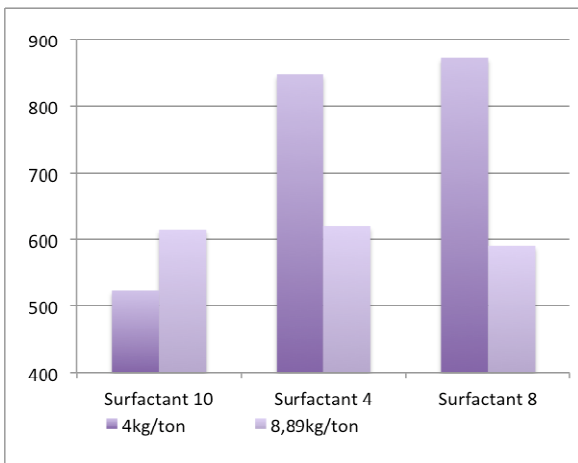


Figure 30. Non-ionic surfactant addition 30g/ton, reject (g)

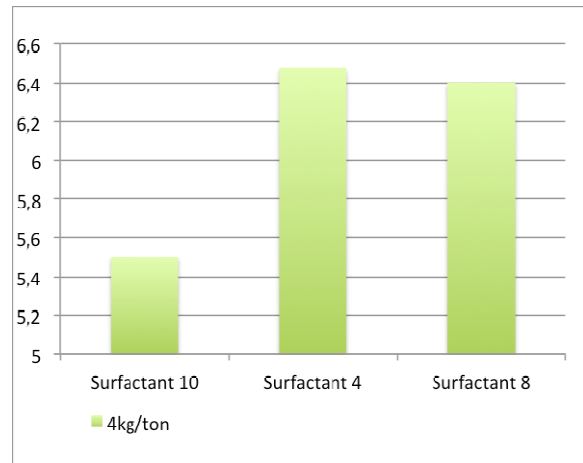


Figure 31. Non-ionic surfactant addition 30g/ton, yield loss (%)

Surfactant and concentration level	Sodium hydroxide concentration	Flotated ERIC	Flotated Brightness	Flotated HW ERIC	Flotated HW Brightness	Unflotated ERIC	Unflotated Brightness	Unflotated HW ERIC	Unflotated HW Brightness
Surfactant 10 30g/ton	Wrong	411,1	54,05	163,1	56,89	1165	42,11	151,2	56,17
Surfactant 10 30g/ton	Right	726,8	47,14	295,5	52,49	1408,1	39,91	312,9	52,3
Surfactant 8 30g/ton	Wrong	386,2	54,39	147,3	56,34	1138	41,17	163,2	56,51
Surfactant 8 30g/ton	Right	386,2	54,39	147,3	56,34	1138	41,17	163,2	56,51
Surfactant 4 30g/ton	Wrong	446,5	53,94	155,1	56,99	1204,7	41,49	173,1	56,89
Surfactant 4 30g/ton	Right	446,6	53,94	155,1	56,99	1204,7	41,49	713,1	56,89

Table 16. All optical properties from sodium hydroxide concentration comparison flotation at 30g/ton

Surfactant	Sodium hydroxide	Δ ERIC	Δ Brightness	Reject (g)	Yield loss (%)
------------	------------------	--------	--------------	------------	----------------

	concentration				
Surfactant 10 30g/ton	Wrong	753,9	11,94	615,4	x
Surfactant 10 30g/ton	Right	681,3	-7,23	522,5	5,503597122
Surfactant 4 30g/ton	Wrong	758,2	12,45	620,7	x
Surfactant 4 30g/ton	Right	788,9	-9,26	847,3	6,474820144
Surfactant 8 30g/ton	Wrong	751,8	13,22	590,9	x
Surfactant 8 30g/ton	Right	787,3	-8,67	872,5	6,402877698

Table 17. Delta values, reject and yield loss.

The comparison of the two levels of NaOH indicates a large difference in results. The result of ERIC is increased and brightness is reduced for all non-ionic surfactants with a lower level of NaOH. The amount of reject from the flotation cell also increases sharply in the case of Surfactant 4 and Surfactant 8, but for Surfactant 10 it actually decreases with a lower NaOH level. The yield loss of Surfactant 10 is also less than that of Surfactant 4 and Surfactant 8 at the lower NaOH level. It is thus comparable to previous results for the non-ionic surfactant at other concentration levels of non-ionic surfactant with higher NaOH addition.

It is worth noting that there is a large time difference between the flotations with the different NaOH levels. This is very important, since the deinkability of paper decreases drastically with time. This subject will be addressed later in a separate point.

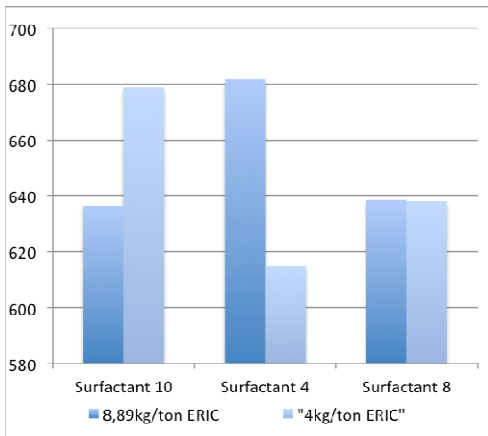


Figure 32. ERIC value, surfactant addition 10g/ton

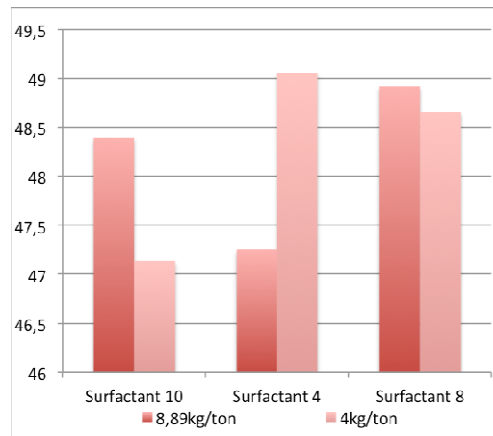


Figure 33. Brightness value, surfactant addition 10g/ton,

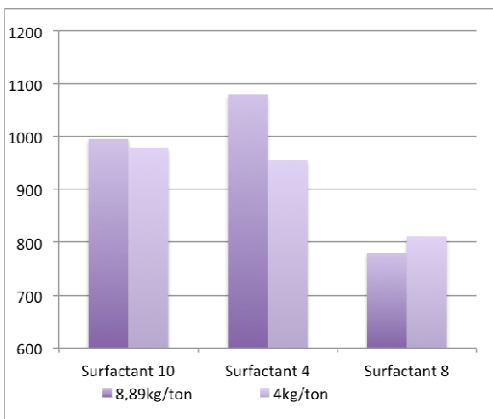


Figure 34. Surfactant addition 10g/ton, reject (g)

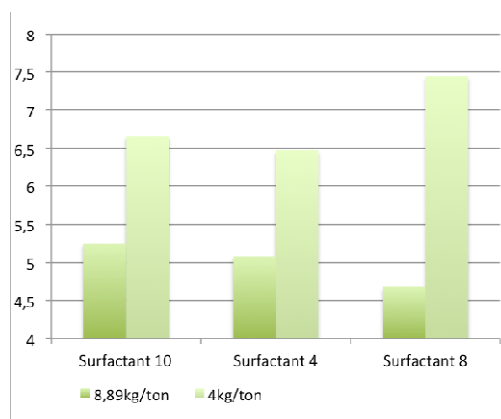


Figure 35. Yield loss(%) Surfactant addition 10g/t

Surfactant and concentration level	Sodium hydroxide concentration	Flotated ERIC	Flotated Brightness	Flotated HW ERIC	Flotated HW Brightness	Unflotated ERIC	Unflotated Brightness	Unflotated HW ERIC	Unflotated HW Brightness
surfactant 10 10g/ton	Wrong	636,5	48,4	254,6	52,85	1386,2	39,93	286,9	52,72
surfactant 10 10g/ton	Right	678,8	47,68	307,6	52,6	1422	40,45	323,9	52,83
surfactant 8 10g/ton	Wrong	638,4	48,92	261,1	53,38	1422,8	37,85	275,5	53,15
surfactant 8 10g/ton	Right	638	48,14	288,3	52,35	1535,7	37,48	316,7	51,72
surfactant 4 10g/ton	Wrong	681,6	47,28	266	53,39	1372,8	40,83	283,3	53,08
surfactant 4 10g/ton	Right	615	49,53	286,8	52,85	1430,7	39,63	307,6	52,27

Table 18. All optical properties from sodium hydroxide concentration comparison flotation at 10g/ton.

Surfactant	Wrong/Right	Δ ERIC	Δ Brightness	Reject (g)	Yield loss (%)
Surfactant 10 10g/ton	Wrong	749,7	8,47	994,5	5,25
Surfactant 10 10g/ton	Right	743,2	7,23	978,9	6,65
Surfactant 8 10g/ton	Wrong	784,4	11,07	779,7	4,67
Surfactant 8 10g/ton	Right	897,7	10,66	810,2	7,44
surfactant 4 10g/ton	Wrong	691,2	6,42	1079,2	5,07
surfactant 4 10g/ton	Right	815,7	9,9	954,3	6,47

Table 19. Delta values, reject and yield loss.

The concentration level of 10g/ton of non-ionic surfactant is the lowest used in these trials. It shows that when kept at a low concentration level, the different surfactant types give fairly different results.

The results show that the decrease in NaOH gives different results for the three s at a low surfactant level. The surfactant 10 gives a better ink removal when used at a higher NaOH concentration and also a higher brightness.

Surfactant 4 is on the contrary affected positively of the lowering in NaOH, with an increased ink removal and higher brightness. Surfactant 8 shows little effect of the lowering of in pH on ERIC and brightness giving the same results independently of NaOH level. The amount of reject did not differ much between the different NaOH additions, however, it is shown that the fibre content of the reject increased at a reduced NaOH level.

The comparison of hyperwashed samples between the two levels of NaOH shows that there is a lower degree of detaching of ink from the paper at a low NaOH level, indicated by the higher ERIC value. The dispersing effect of the non-ionic surfactant also increases by the lower level of NaOH, giving higher ERIC value of unflotated pulp, indicating that the agglomeration at a lower pH is lower then at higher levels. There is no indication that the brightness should be affected by the lower pH. This may be due to the relatively low decrease in pH.

Surfactant and concentra-	Sodium hydroxide concentra	Flotated ERIC	Flotated Brightness	Flotated HW ERIC	Flotated HW Brightness	Unflotated ERIC	Unflotated Brightness	Unflotated HW ERIC	Unflotated HW Bright-
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Surfactant	Surfactant concentration	Surface tension	Surface energy	Surface free energy	Surface enthalpy	Surface entropy	Surface Gibbs free energy	Surface Helmholtz free energy	Surface enthalpy of activation	Surface entropy of activation	Surface Gibbs free energy of activation	Surface Helmholtz free energy of activation
Surfactant 10 30g/ton	Right	726,8	47,14	295,5	52,49	1408,1	39,91	312,9	52,3			
Surfactant 10 10g/ton	Right	678,8	47,68	307,6	52,6	1422	40,45	323,9	52,83			
Surfactant 8 30g/ton	Right	386,2	54,39	147,3	56,34	1138	41,17	163,2	56,51			
Surfactant 8 10g/ton	Right	638	48,14	288,3	52,35	1535,7	37,48	316,7	51,72			
Surfactant 4 30g/ton	Right	446,6	53,94	155,1	56,99	1204,7	41,49	713,1	56,89			
Surfactant 4 10g/ton	Right	615	49,53	286,8	52,85	1430,7	39,63	307,6	52,27			

Table 20. Comparison of concentration at right Sodium hydroxide concentration

Comparing the results at the low level of NaOH (low) at 10 g/t and 30 g/t non-ionic surfactant shows that the lower non-ionic surfactant dosage does not perform as well as 30 g/t. Thus, there exists a lower limit for the concentration. It should be noted that the experiments at 10 g/t were performed with old newsprint, however the relative difference in the results from the two non-ionic surfactant levels should be significant.

4.4. CMC in process water

CMC values were measured in the process water for some of the non-ionic surfactants in order to compare with the CMC measured in milliQ water to see if a correlation factor could be found. The factor could help with dosing in the process, to avoid overdosing and thereby creating sterically stable colloidal ink particles. The measurement apparatus was the same as used in the other CMC measurements. The measurements are shown in appendix VI.

The results from the graphs in show that the initial surface tension of the process water is low, due to surface-active materials, which makes it difficult to find a CMC. However, one can tell that there is a big difference in the shape and level of the CMC curve for process water compared to MilliQ water. This may be a reason why the difference in the performance between surfactants with e.g. very different HLB and cloud point is smaller than expected

4.5 Calculation of the theoretical amount of surfactant

The lowest possible amount of non-ionic surfactant for coverage of ink particles was theoretically calculated. The base of the calculations was that the surface of all ink particles was to be covered by non-ionic surfactant and that no other surface was to adsorb any non-ionic surfactants until the ink was all covered.

The ink particles were assumed to be spherical in shape and to have a diameter of $1-15\mu\text{m}^{35}$. The amount of ink was assumed to be 0,5-2% of the total weight of the newspaper and magazine and density of ink was set to $1099,4\text{ kg/m}^3$.

Further on, the area covered by a single non-ionic surfactant was assumed to be 10^{-16}m^2^{36} .

The calculations were conducted for Surfactant 4, Surfactant 8 and Surfactant 9. Surfactant 10 was excluded from calculations because of the lack of data on the molecular weight.

Surfactant	Assumptions	Calculated amount surfactant g/ton paper	Max/min amount calculated
Surfactant 4	2 weight % ink, Ink particle $1\mu\text{m}$	4,5311	Max
Surfactant 4	0,5 weight % ink, Ink particle $15\mu\text{m}$	0,0755	Min
Surfactant 8	2 weight % ink, Ink particle $1\mu\text{m}$	1,5859	Max
Surfactant 8	0,5 weight % ink, Ink particle $15\mu\text{m}$	0,0264	Min

Surfactant 9	2 weight % ink, Ink particle 1µm	0,4712	Max
Surfactant 9	0,5 weight % ink, Ink particle 15µm	0,0078	Min

Table 21. Summary of theoretical amount of surfactant (see appendix IX. for complete calculations)

The calculated amounts of non-ionic surfactant are low compared to the dosage levels used in practical flotations. There is also a large span of additions levels from the lowest of Surfactant 9 at 0,5 weight % and particle size of 15µm and the highest level of Surfactant 4 with 2 weight % and ink particle size of 1µm. The difference of four orders of magnitude in the calculations shows the influence of the assumptions on the theoretical addition levels. In reality, one must take into account the effect of surfactants adhering to other surfaces than the ink particles. For example, the use of 10 g/ton of Surfactant 4 proved to give fairly good flotation results and thus shows that the level of 4 g/ton is not an unrealistic addition level. However, increasing the dosage further to 30 g/ton improved the results, which shows that the surfactant levels in practice must be much higher than can be found from theoretical calculations.

4.6 Ageing effects of the ink

The ageing effects on the paper gives different absolute values between the trials performed in the beginning of the study and the later ones performed some months later and the ones performed earlier. With this in mind, it has been tried to only compare trials within the same series of experiments.

The results seen over time deteriorated for all the surfactants. As described earlier, this is caused by cross-linking effects within the ink and between the ink and the fibre, making deinking of aged paper more difficult.

4.7 The effect of surfactant properties on the flotation results

The effect of surfactant properties parameters on the flotation results is not clear, even if some conclusions may be drawn. The relatively small difference in the results may be a result of the process-like environment, which makes the non-ionic surfactants behave differently than in pure water (as can be seen from the CMC curves).

4.7.1. Effect of chemical structure and molecular weight

The chemical structure of the non-ionic surfactant, which gives rise to its properties, is an important factor. The flotations show that the choice of EO/PO based surfactants, as indicated by literature, is a good starting point for choice of non-ionic surfactant. The most successful non-ionic surfactants during the initial trials were EO/PO based. Also, block copolymers based on EO/PO performs well.

The molecular weight is also an important parameter, since the non-ionic surfactants with lower molecular weight were found to give a large amount of reject. It was shown in the initial trial that these small and “aggressive” non-ionic surfactants, with molecular weight of less than 1000 g/mol, gave a higher level of reject than non-ionic surfactants with higher molecular weight. They also performed worse in terms of higher ERIC and lower brightness values.

4.7.2. Concentration effects

Various concentrations corresponding to different positions in the CMC curves were evaluated for some of the non-ionic surfactants. There were indications of that the increase in concentration of non-ionic surfactant above a certain level did not give an improvement in results. In some flotations there was even a decrease in removed ink. This could be the result of sterically stability of the ink

particles and thus a reduced amount of ink attached to the air bubbles in flotation. On the other hand, a lower limit for the concentrations also seems to exist. The empirically derived amount of approx. 30 – 50 g non-ionic surfactant per ton of dry fibre seems to be most favourable also in these studies, whereas experiments with both 10 and 100 g/ton fall outside the optimal dosage range. There is also a change in non-ionic surfactant concentration during the course of the experiments. The concentration level is higher in the pulping stage than in the flotation stage. The concentrations levels are always over the CMC of the non-ionic surfactants in the pulping stage of the process, whereas in the flotation step the concentration is below CMC. This may in turn influence the dispersing effect of the non-ionic surfactant. Thus, one may consider comparing additions of non-ionic surfactant at different steps in the deinking process.

4.7.3. Cloud point and HLB

The cloud point of the various surfactants was considered during the flotations. According to literature, a process temperature above this surfactant specific temperature would decrease the ability of the non-ionic surfactant to disperse ink particles. Since the temperature in a deinking mill for practical reasons vary between 45°C - 55°C, non-ionic surfactants were chosen that had cloud points above, close to and below this temperature range.

The flotations were kept above the cloud point of Surfactant 8 (33°C) during all trials. Although the HLB of Surfactant 8 is 4, indicating that this non-ionic surfactant would have poor dispersing ability³⁷, this non-ionic surfactant yet showed good results in the trials. The non-ionic surfactant used below its cloud point (Surfactant 4, cloud point 70°C) performed even better, but it is not clear if this was due to the difference in cloud point or in HLB (HLB=12 for Surfactant 4). The fatty polyether surfactant number 10 with a cloud point of 44°C, i.e. close to the process temperature (HLB unknown) also has a similar performance. Both Surfactant 4 and Surfactant 10 are commercial non-ionic surfactants frequently used for deinking purposes, in spite of their difference in cloud point. It is likely that in a practical system, other factors would have larger impact on the flotation performance, and neither the surfactant HLB value nor the cloud point would be considered critical parameters.

It is worth noticing that the cloud point may be affected by the ionic strength of the system. However, in screening experiments it was found that the amount of salt needed in order to lower the cloud point with a few degrees by far exceeded the salt content in the current laboratory system. Thus, the non-ionic surfactant cloud points may be considered to be relatively unaffected under the conditions in this study.

5. Conclusions and future work

Deinking flotation is a complex process with a high degree of uncertainty. Many factors may affect the results; some of which can be controlled (such as temperature and concentration of reagents) and some that are difficult to control (e.g. ageing effect of paper and the human factor when handling the cell).

This study showed that the traditional flotation formula using a fatty acid emulsion for ink detachment and flotation could be replaced with a balanced amount of a correctly selected non-ionic surfactant while retaining deinking efficiency. An unexpected positive effect was that although the total amount of reject increased in the non-ionic surfactant trials, the amount of solid material in the reject decreased, leading to a higher total yield of fibre and filler material. This means that a correct use of the non-ionic surfactant could give important economical benefits compared to the use of a fatty acid emulsion.

The experiments indicated which parameters that were most important in the selection of a non-ionic surfactant for deinking. The use of fairly large, non-ionic surfactants with a molecular weight of several thousand g/mol turned out to be favorable. The non-ionic surfactants based on ethylene oxide/propylene oxide (EO/PO) appeared to give an advantage in the flotations, which was in accordance with literature. Very low molecular weight non-ionic surfactants showed good ink detachment but were unsuitable for ink removal in the flotation step, also producing large amounts of reject. The non-ionic surfactant that showed the best overall results throughout the experiments was Surfactant 4, an EO/PO surfactant with a high molecular weight designed for flotation deinking. However, other non-ionic surfactants such as Surfactant 8 (a PO/EO block copolymer, also with a high molecular weight, >5000), the ethoxylated fatty alcohol Surfactant 5, and the fatty acid ester of a poly(ethylene glycol) Surfactant 10 also performed well and may be interesting alternatives. A combination of different non-ionic surfactants could be considered as a subject for future studies.

The non-ionic surfactant dosage frequently used in industry, of the order of 30 – 50 g non-ionic surfactant per ton of dry fibre, seems to be a balanced choice. Higher dosages exceeding the CMC increases the amount of reject, whereas too low dosages give insufficient deinking efficiency. Since the CMC curve is easily affected by many factors (process contaminations, temperature variations etc.), it cannot be used as a universal guidance for dosing. The same is the case for both the cloud point and the HLB values. These parameters seemed not to be crucial for the deinking performance.

As has been indicated in this study, the alkali dosage could affect the performance of the non-ionic surfactants. This may be linked to the research field of semi-neutral deinking, using alternative alkaline sources. The effect of non-ionic surfactants on the deinking performance under these very different conditions may also be the subject for future studies.

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Appendices

Appendix 0. Recipe for pulping

1. Shred 278 g of paper to approximately 2×2 cm pieces. The proportions of paper should be 194,6g (70%) ONP and 83,4g (30%) OMG. Add the paper to the Kitchen Aid bowl.
2. Measure the concentration of the hydrogen peroxide according to the method described in Appendix II.
3. Add 1,625dm³ hot tap water to the Kitchen Aid bowl and then the chemicals according to recipe. The chemicals are mixed into some of the hot tap water to facilitate the addition.

Dosage in the process	Dosage in the pulper
NaOH: 7,0kg/1000kg = 0,7%	2,47g(at 45% concentration)
Na ₂ SiO ₃ : 12,5kg/1000kg = 1,25%	8,92g(at 39% dry content)
H ₂ O ₂ : 8,0kg/1000kg = 0,8%	22,24g(at 10% concentration)
Surfactant: 30g/1000kg = 0,003%	X mg (to be varied)

Table 22. Pulper chemicals dosage

4. A surfactant solution of 1g surfactant/100g hot tap water is prepared and heated to disperse the surfactant evenly. From this stock solution the right amount of surfactant is then added.
5. Run the Kitchen Aid on speed 2 for 20min.
6. Fill the Kitchen Aid bowl with additional hot tap water until it reaches approximately 1 cm from the edge of the bowl. Transfer the bowl to the oven and let rest there at 56-57°C for 30 minutes.
7. Prepare the chemicals for addition into the flotation cell.

Dosage in the process	Dosage in the pulper
Emulsion: 2,5kg/1000kg =0,25%	9,93g(at 0,07%)
CaCl ₂	2,25g(100% dry content) dispersed in water

Table 23. Flotation chemicals dosage

8. Weight the container for collecting the reject.
9. Take the pulp from the oven and add half of the pulp to the disperser container and fill with hot tap water. Disperse for 3 minutes and then add to the flotation cell. Repeat with the rest of the pulp. During the dispersion, rinse the tap water to acquire a temperature of 50-60°C and heat the prepared emulsion until it is completely melted. Fill a squirt bottle with hot tap water.
10. Add the melted soap and then add hot tap water up to the 23dm³ marker on the flotation cell. Note the temperature.
11. **Flotation:** Fasten the foam separation detail and start the swirling. Collect a sample of 2 dm³ unflotated pulp. Then add hot tap water until the 23 dm³ mark. Add the dispersed CaCl₂ to obtain a water hardness of 10 dH°.

12. **Start the flotation and the stopwatch at the same time.** Adjusting the control from swirl to air starts the flotation. Rinse the walls of the cell with the squirt bottle during the flotation. Refill if empty. Run the flotation for six minutes
13. After six minutes, turn of the flotation but keep the swirl on. Take out 200ml slush to rinse the nozzle with fresh flotated pulp. Collect a 2dm³ sample in a separate container. Then turn off the swirl and empty the flotation cell.
14. Note the flow of air, amount of water used and amount of reject.
15. Analyse the pulp and reject.

Appendix I. Hydrogen peroxide concentration determination

The rate at which the experiment is carried out affects the quality of results so that a rapid procedure is to desired for an accurate result. This is due to the decomposition of hydrogen peroxide.

1. Fill 100ml of distilled water into a beaker
2. Add approximately 0,5g of the hydrogen peroxide you want to determine the concentration of, note the exact weight
3. Add 5ml of 1M potassium iodide (KI), 5ml of 2M sulphuric acid (H₂SO₄) and approximately 10 drops of ammonium molybdate
4. Titrate with 0,1M thiosulphate (Na₂S₂O₃) until the solution is clear.

The concentration is then acquired from the following formula:

$$\text{Hydrogen peroxide Concentration (g/dm}^3\text{)} = \frac{\text{ml of titrated thiosulphate} \times 0,1 \times 34,02}{2 \times \text{exact weight of added hydrogen peroxide}}$$

Appendix II. Preparation of samples and hyperwash

The samples collected need to be prepared for optical analyses. The sample made from each flotation were:

1. Flotated pulp

Take $0,4\text{dm}^3$ of the 2dm^3 . Suction filtrate the sample.

2. Flotated pulp Hyperwashed

Take $0,5\text{ dm}^3$ of the 2dm^3 sample from the cell. Hyperwash and the suction filter the sample.

3. Unflotated pulp

Take $0,3\text{ dm}^3$ of the 2dm^3 sample from the cell and add a drop of polyethyleneimine. Stir until reaction finished. Suction filter the sample.

4. Unflotated pulp Hyperwashed

Take $0,5\text{ dm}^3$ of the 2dm^3 sample from the cell. Hyperwash and the suction filter the sample.

Filter paper was placed on top of the samples. The samples were then put under pressure of 4,5 bar for 3 minutes. The back of the filter paper was the flipped to prevent it from sticking to the sample. They were the put in a drier for 60 minutes and then analysed with the optical equipment.

Hyperwash

The container was filled to $\frac{3}{4}$ with tap water, with the bottom nozzle closed; thereafter the sample was poured in. After 1 minute the bottom nozzle was opened and fresh water was added in the top to keep a constant level. After 20 dm^3 had been flushed through the washer the washed pulp is scraped of the filter and dispersed in $0,4\text{ dm}^3$ water.

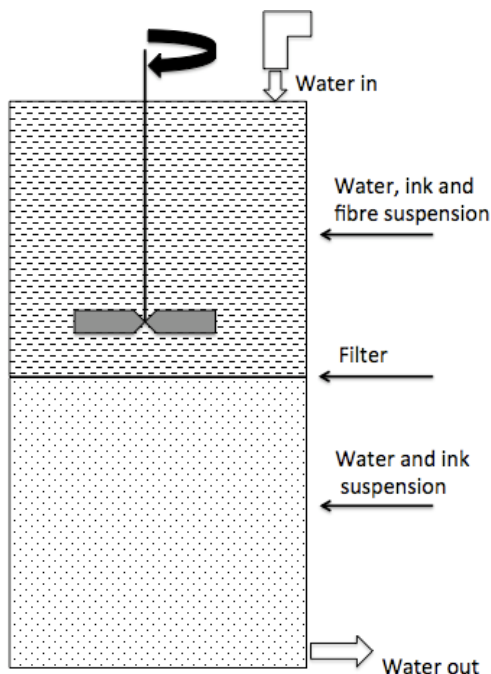


Figure 36. Hyperwash setup

Appendix III. Yield measurements

The exchange of the flotation was obtained through the amount of dry reject.

The wet reject was placed to separate to some degree, solid and liquid, and the suction filtered in the same way as the samples above.

After obtaining a cake of reject through suction filtration, the cake was then further dried in an oven in approximately 100°C over night.

The dry reject was the weighted.

Yield was then obtained through the following formula:

$$Yield = \frac{\text{Dried reject}}{\text{Dry weight of ONP + OMP}} \times 100$$

Appendix IV. Chemicals addition in all the flotations.

Type of surfactant	Name	Surfactant (mg)	Emulsion (g)	NaOH 45% (g)	H ₂ O ₂ (g)	NaSiO ₃ (g)	Soap (g)	CaCl ₂ (g)
Surfactant 1	100805	8,6	X	5,41	29,63 (75,33g/dm ³)	8,9(39% T.H.)	10,2	2,55
Surfactant 2	100806	8,3	X	5,48	30 (73,3 g/dm ³)	8,9(39% T.H.)	10,2	2,56
Surfactant 3	100809	8,2	X	5,41	25,65 (86,7g/dm ³)	8,9(39% T.H.)	10,2	2,55
Surfactant 4	100811 flot 2	8,3	X	5,44	29,78 (74,8g/dm ³)	8,9(39% T.H.)	10,2	2,5
Surfactant 5	100810	8,24	X	5,41	26,62 (84,0 g/dm ³)	8,9(39% T.H.)	10,2	2,49
Surfactant 6	010816	8,3	X	5,45	25,7 (86,5 g/dm ³)	8,5(41,19%TH)	10,2	2,5
Surfactant 7	100818 flot 1	8,5	X	5,41	23 (96,5 g/dm ³)	8,4(41,19%TH)	10,2	2,5
Surfactant 8	100818 flot 2	8,2	X	5,48	23,7 (96,5 g/dm ³)	8,4(41,19%TH)	10,2	2,5
Surfactant 9	100817 flot 2	8,4	X	5,44	24,09 (96,5 g/dm ³)	8,4(41,19%TH)	10,2	2,5
Surfactant 10	100817 flot 1	9,8(82,5% TH)	X	5,45	24,7 (89,9 g/dm ³)	8,4(41,19%TH)	10,2	2,5

Table 24. Screening trials

Type of surfactant	Name	Surfactant (mg)	Emulsion (g)	NaOH 45% (g)	H ₂ O ₂ (g)	NaSiO ₃ (g)	Soap (g)	CaCl ₂ (g)
Reference	101006 flot 2	X	4,7	5,5	24,58 (90,8g/dm ³)	8,8 (39% T.H.)	9,6	2,6
surfactant 4 (30g/ton)	100811 Flot 2	8,3	X	5,44	29,78 (74,8g/dm ³)	8,9 (39% T.H.)	10,2	2,5
surfactant 4 (50g/l)	100915	13,9	X	5,46	32,7 (68g/dm ³)	8,5 (41,19%TH)	9,3	2,5
surfactant 4 (100g/l)	100916 Flot1	27,8	X	5,51	25,56 (87g/dm ³)	8,6 (41,19%TH)	9,4	2,5
surfactant 4 (300g/l)	100916 Flot2	83,4	X	5,46	25,56 (83,3g/dm ³)	8,5 (41,19%TH)	9,2	2,5
surfactant 4 (50mn/m)	100915	13,9	X	5,46	32,7 (68g/dm ³)	8,5 (41,19%TH)	9,3	2,5
surfactant 8 (50mn/m)	100929	5,6	X	5,53	28,58 (77,8g/dm ³)	8,4 (41,19%TH)	9,2	2,5
surfactant 9 (50mn/m)	100928	2,53	X	5,47	28,5 (78,1g/dm ³)	8,42 (41,19%TH)	9,4	2,65
surfactant 10 (50mn/m)	101004	2,99(82,5% TH)	X	5,7	29,4 (75,7g/dm ³)	8,5 (41,19%TH)	9,2	2,5
surfactant 9 (100g/ton)	100928	2,53	X	5,5	28,5 (78,1g/dm ³)	8,4 (41,19%TH)	9,4	2,65
surfactant 10 (100g/ton)	101004	2,99(82,5% TH)	X	5,7	29,4 (75,7g/dm ³)	8,5 (41,19%TH)	9,2	2,5
surfactant 8 (100g/ton)	101006 flot1	2,78	X	5,6	24,54 (90,83g/dm ³)	8,5 (41,19%TH)	9,3	2,6
surfactant 4 (100g/ton)	100916 flot1	27,8	X	5,51	25,56 (87g/dm ³)	8,6 (41,19%TH)	9,4	2,5

Table 25. Concentration effects

Type of surfactant	Name	Surfactant (mg)	Emulsion (g)	NaOH 45% (g)	H ₂ O ₂ (g)	NaSiO ₃ (g)	Soap (g)	CaCl ₂ (g)
surfactant 10 (wrong, 10g/ton)	10101 1 flot 1	3,4 (82,5% TH)	X	5,5	26,7 (83,3g/dm ³)	8,5(41,19%TH)	10	2,5
surfactant 4 (wrong, 10g/ton)	10101 1 flot 2	2,8	X	5,7	26,8 (83,3g/dm ³)	8,4(41,19%TH)	10	2,5
surfactant 8 (wrong, 10g/ton)	10101 2 flot1	2,8	X	5,5	27,2 (81,6g/dm ³)	8,5(41,19%TH)	10	2,5
surfactant 10 (right, 10g/ton)	10101 3 flot 2	3,4 (82,5% TH)	X	2,5	26,2 (83,5g/dm ³)	8,5(41,19%TH)	10	2,5
surfactant 4 (right, 10g/ton)	10101 2 flot 3	2,8	X	2,5	24,4(81,6g/dm ³)	8,6(41,19%TH)	10	2,5
surfactant 8 (right, 10g/ton)	10101 2 flot 2	2,8	X	2,5	24,3 (91,5g/dm ³)	8,5(41,19%TH)	10	2,5
surfactant 10 (right, 30g/ton)	10101 4 flot 2	10,1 (82,5% TH)	X	2,5	25,6 (87,0g/dm ³)	8,5(41,19%TH)	10	2,5
surfactant 4 (right, 30g/ton)	10101 4 flot 1	8,34	X	2,5	25,6 (87,0g/dm ³)	8,5(41,19%TH)	10	2,6
surfactant 10 (wrong, 30g/ton)	10081 7 flot 1	9,8 (82,5% TH)	X	5,45	24,7 (89,9 g/dm ³)	8,41(41,19%TH)	10,2	2,5
surfactant 4 (wrong, 30g/ton)	10081 1 flot 2	8,3	X	5,44	29,78 (74,8g/dm ³)	8,91(39% T.H.)	10,2	2,5
surfactant 8 (wrong, 30g/ton)	10081 8 flot 2	8,2	X	5,48	23,7 (96,5 g/dm ³)	8,43(41,19%TH)	10,2	2,5

Table 26. Right against wrong dosage levels of sodium hydroxide

Appendix V. CMC measurement method

The CMC was measured accordingly.

1. Preparation of stock solution of surfactant and MilliQ/Process water. The concentration of the stock solution was chosen to be at the CMC and 1dm^3 of this solution was prepared.
2. The automatic pipette used to add stock solution to the measurement beaker was rinsed with $0,4\text{dm}^3$ stock solution to ensure the right concentration of the concentration through the entire system of the pipette
3. The temperature was set to the experiment specific for current experiment at the heating equipment.
4. A beaker cleaned with ethanol, de ionized water and dried with a Kleenex wipe was filled with 10ml of milliQ/process water.
5. After set-up of the laboratory equipment for the experiment the right data was feed into the computer; surrounding phase, liquid phase, starting volume in measurement beaker, concentration of surfactant in stock solution and concentration span. The minimum practically addition level is around 0,01ml.
6. The pipe used to add stock solution to the measurement beaker need to be checked regularly in case of slipping from the fixture.
7. When the measurement is finished rinse the automatic pipette with 800ml of deionized water.

Appendix VI. CMC measurements in MilliQ water.

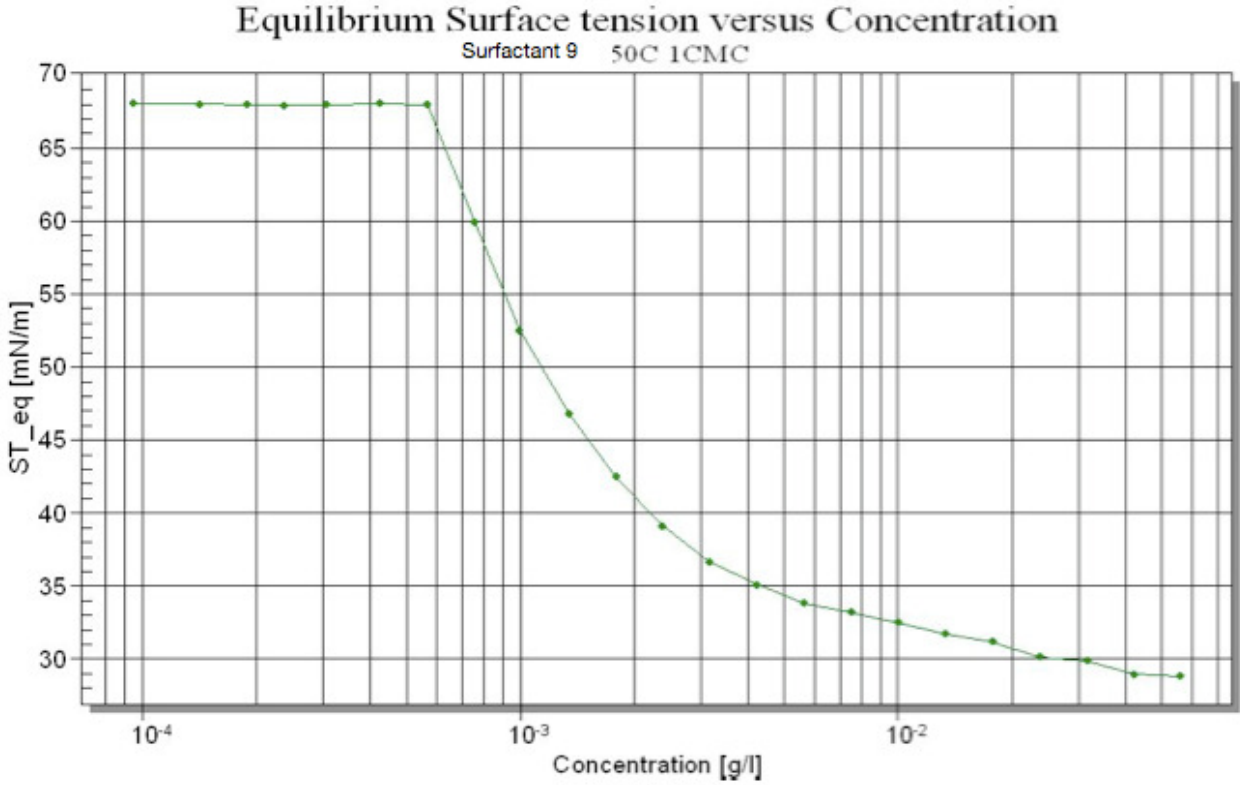


Figure 37. CMC measurements of surfactant 9

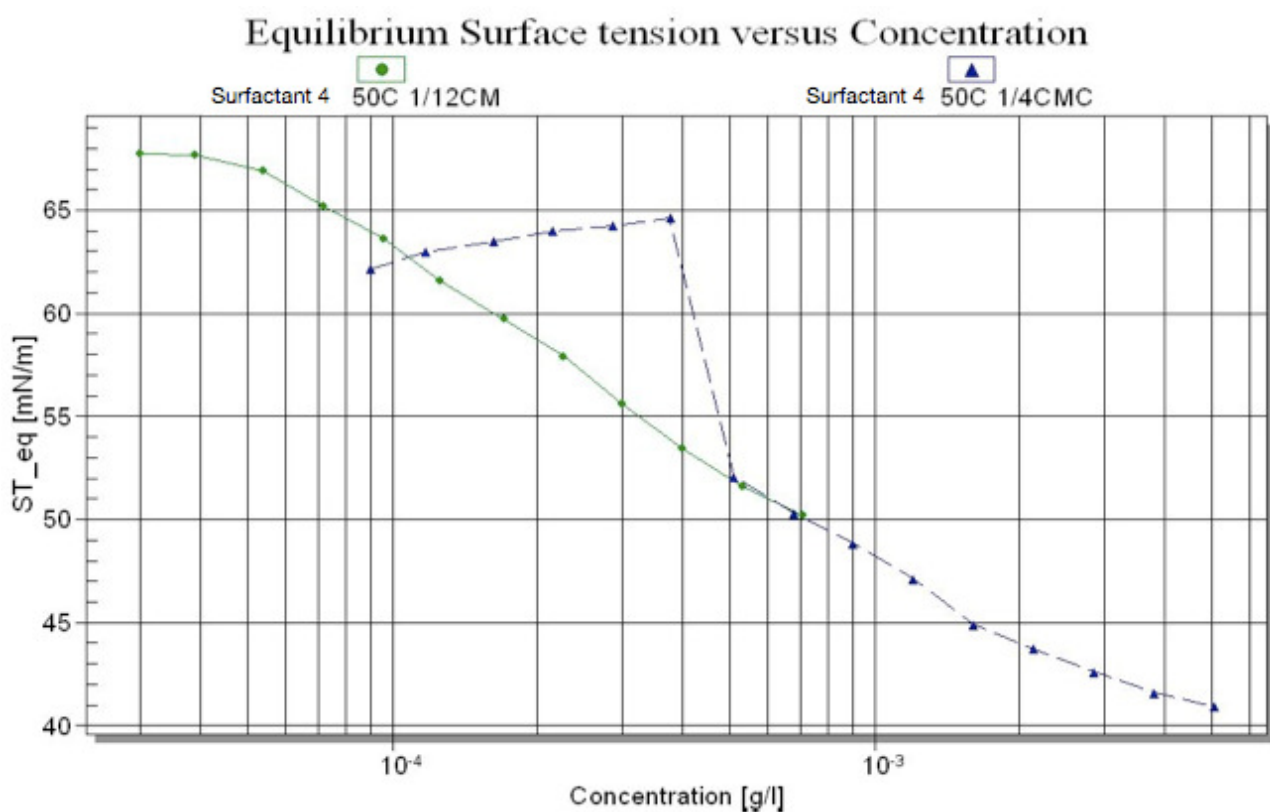


Figure 38. The CMC measurement of Surfactant 4

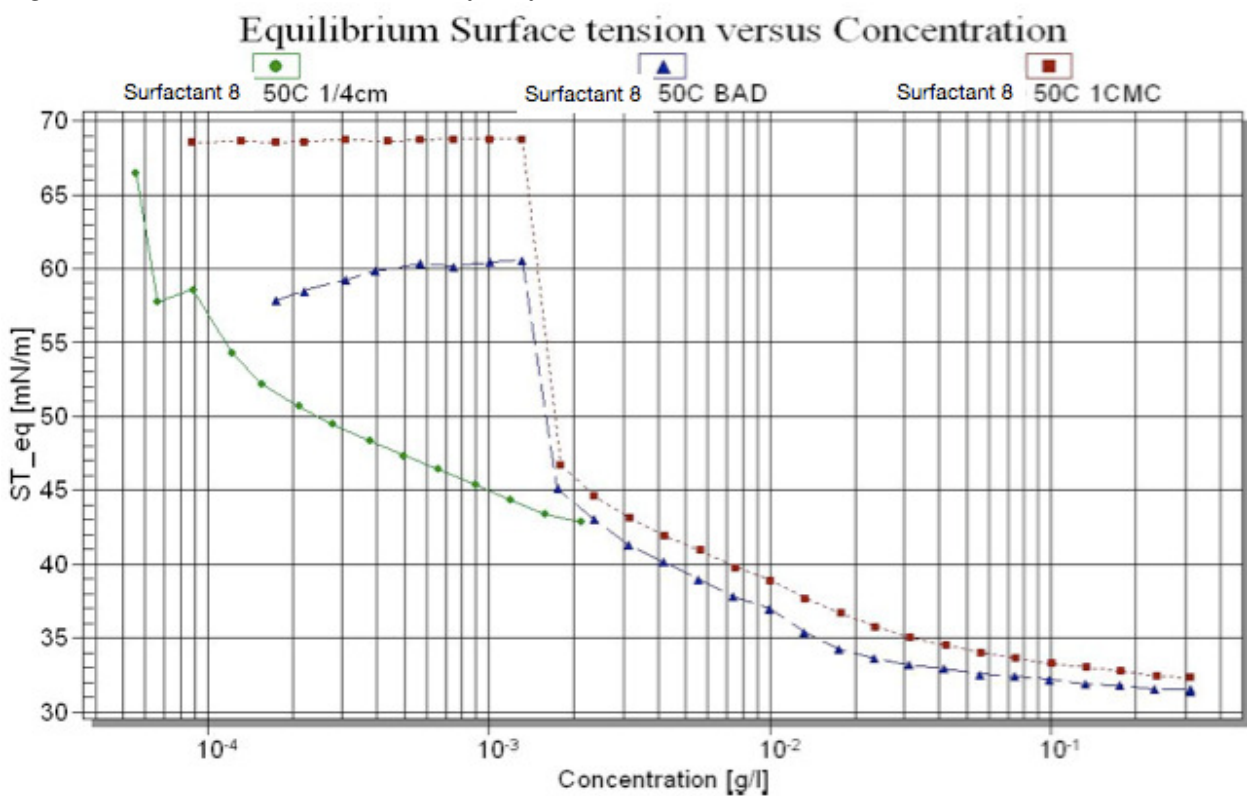


Figure 39. CMC measurements of surfactant 8

Equilibrium Surface tension versus Concentration

Surfactant 10

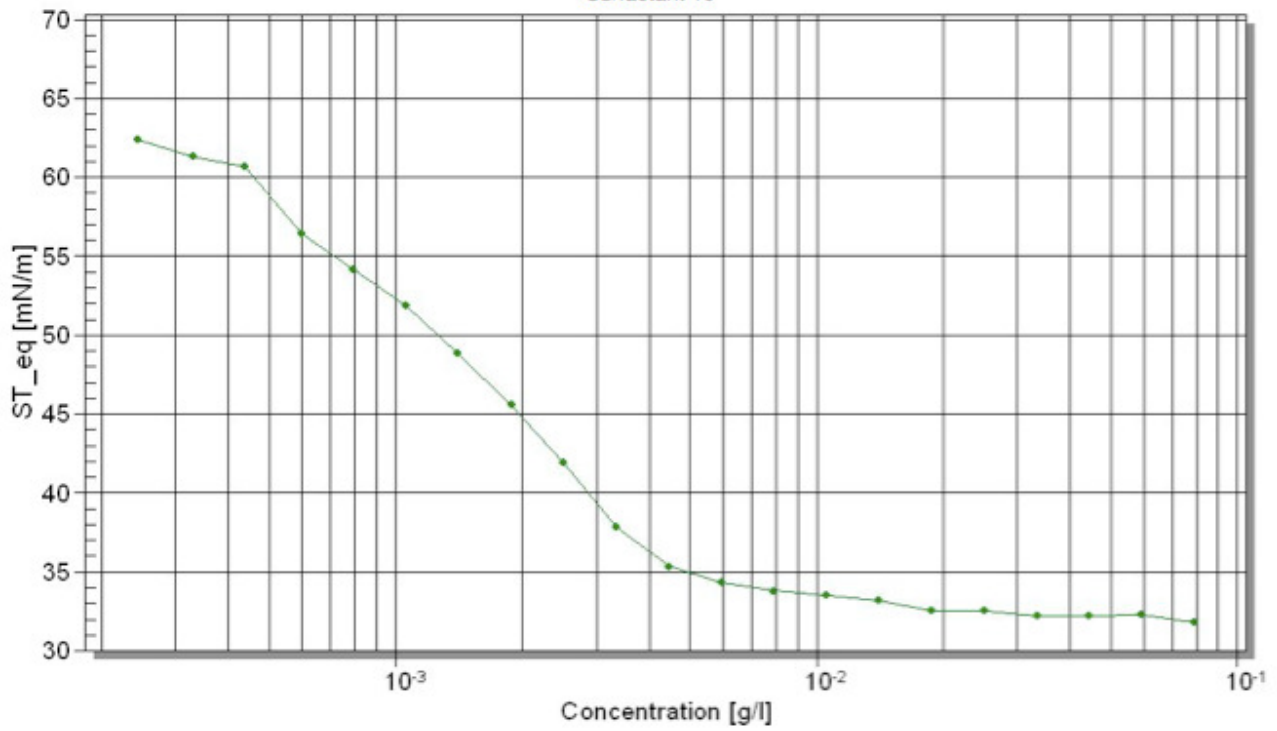


Figure 40. CMC measurements in surfactant 10

Surfactant 10 **PW**

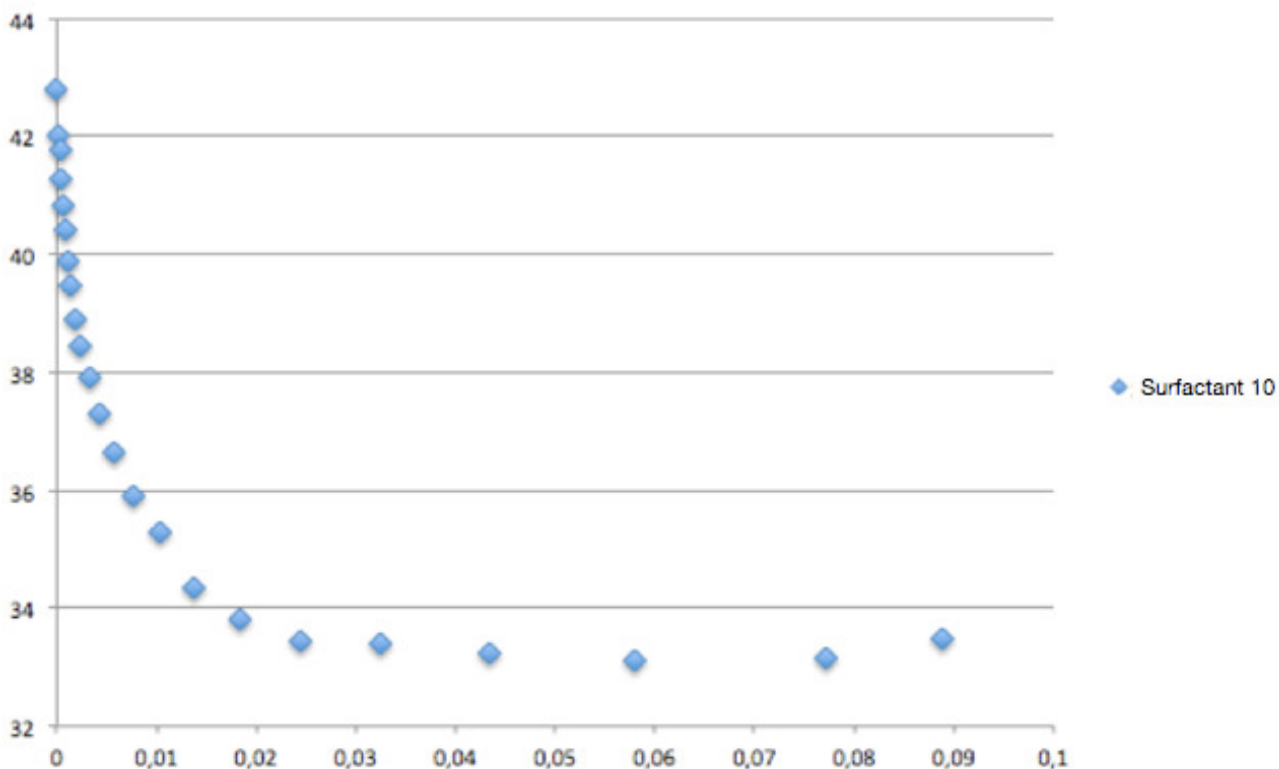


Figure 43. CMC curve for surfactant 10, in process water (PW). Concentration (g/l) and surface tension (mN/m) on axis.

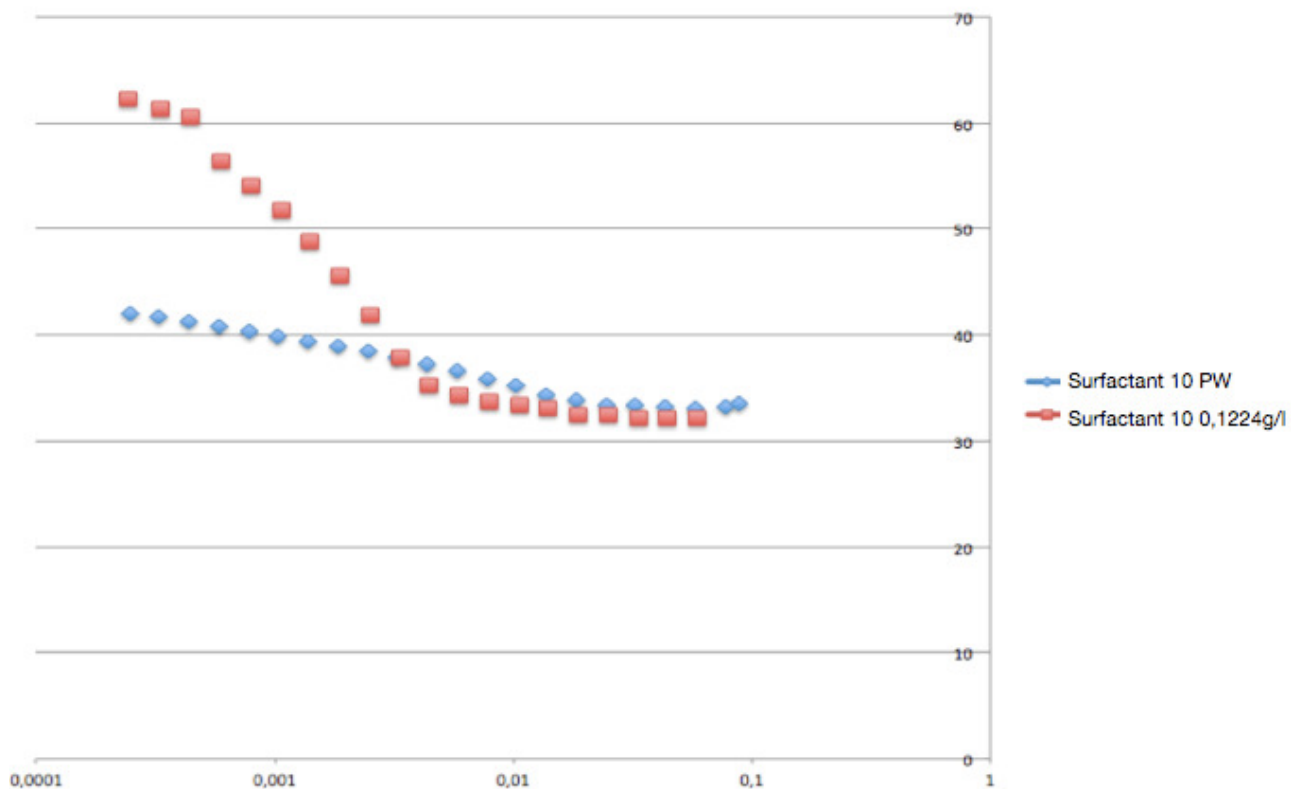


Figure 44. CMC curve for surfactant 10, in process water (PW) and MilliQ water. Concentration (g/l) and surface tension (mN/m) on axis.

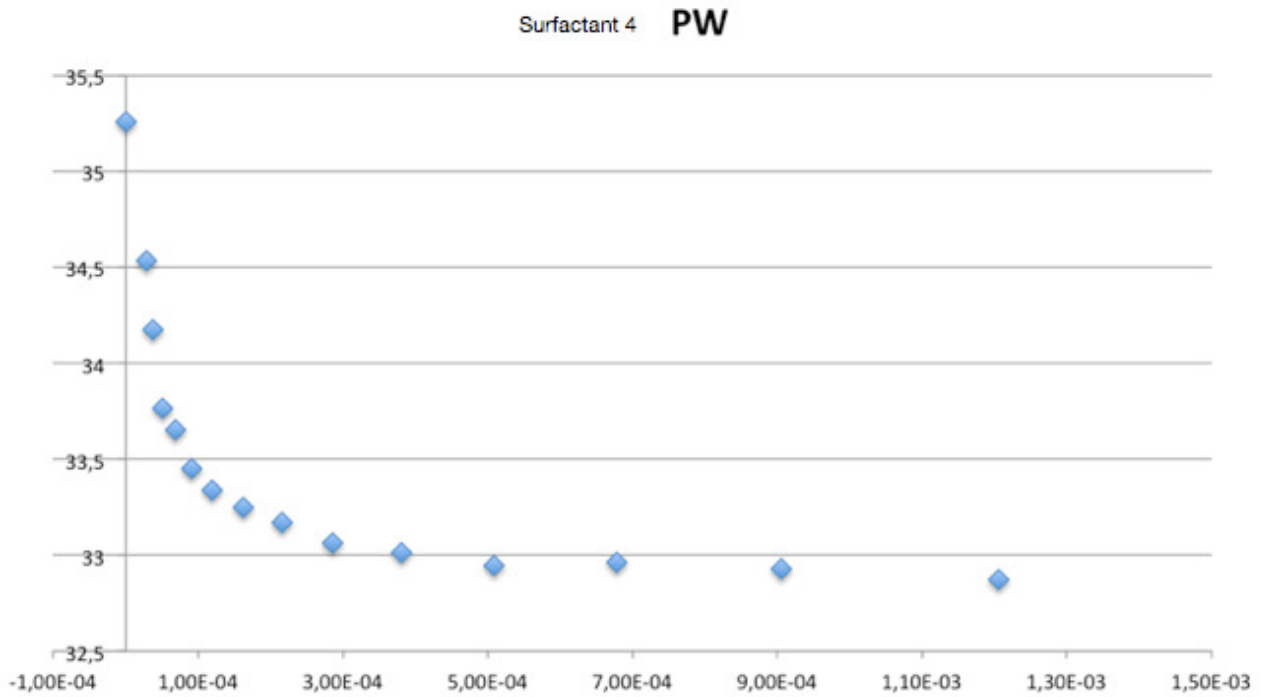


Figure 45. CMC curve for surfactant 4, in process water (PW). Concentration (g/l) and surface tension (mN/m) on axis.

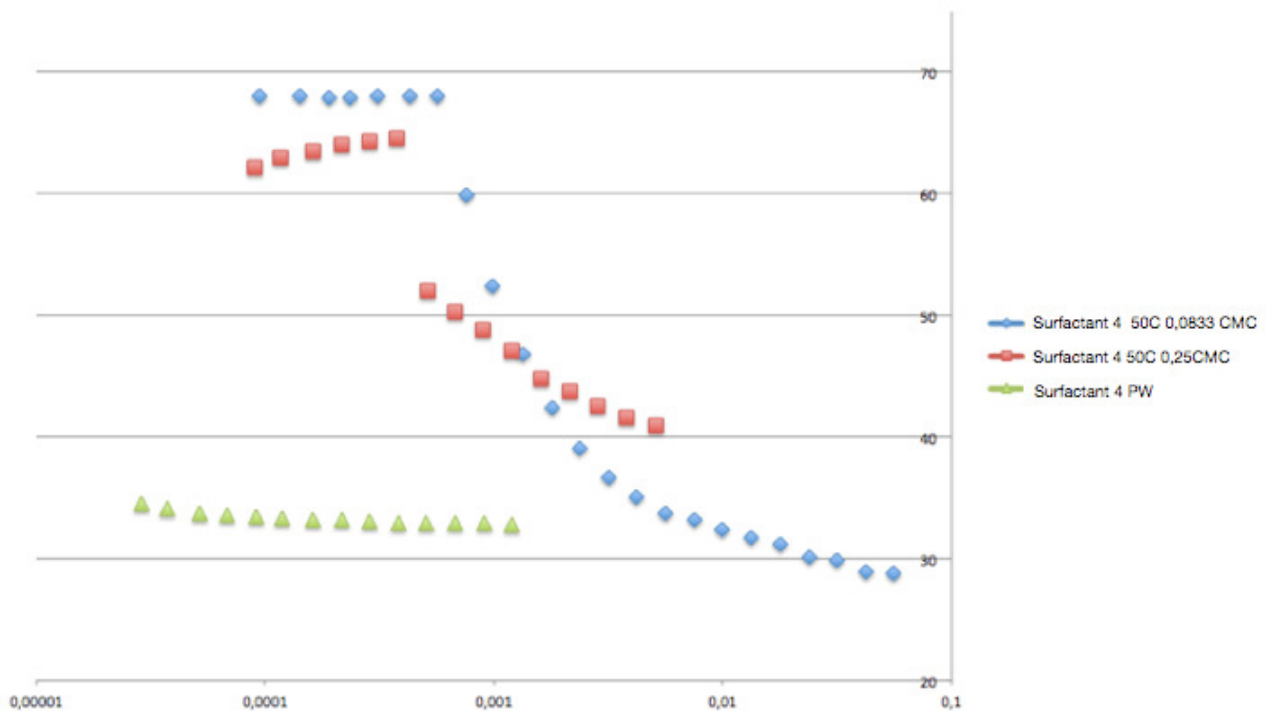


Figure 46. CMC curve for surfactant 4, in process water (PW) and milliQ water. Concentration (g/l) and surface tension (mN/m) on axis.

Appendix VIII. The pH calculation

Addition:

Case 1. 5,45g 45% NaOH = 2,4525g NaOH

Case 2. 2,5g 45% NaOH = 1,125g NaOH

Molar mass of NaOH = 39,99g/mol

Water in pulper = 1,625dm³

Water in flotation = 23dm³

$$pOH = -\log_{10} \frac{[OH^-]}{mol \times dm^3}$$

$$pH + pOH = 14$$

Case 1:

$$\frac{2,45g NaOH}{39,99g/mol} = 0,061mol OH^-$$

$$[OH^-]_{pulper} = \frac{0,061mol}{1,625dm^3} = 0,0375mol/dm^3$$

$$pOH_{pulper} = -\log_{10} \frac{0,0375mol}{dm^3} = 1,4259$$

$$pH_{pulper} = 14 - 1,4259 = 12,57$$

$$[OH^-]_{flot} = \frac{0,061mol}{23dm^3} = 0,00265mol/dm^3$$

$$pOH_{flot} = -\log_{10} \frac{0,00265mol}{dm^3} = 2,5767$$

$$pH_{flot} = 14 - 2,5767 = 11,42$$

Case 2:

$$\frac{1,125g NaOH}{39,99g/mol} = 0,028mol OH^-$$

$$[OH^-]_{pulper} = \frac{0,028mol}{1,625dm^3} = 0,0173mol/dm^3$$

$$pOH_{pulper} = -\log_{10} \frac{0,0173mol}{dm^3} = 1,7616$$

$$pH_{pulper} = 14 - 1,7616 = 12,24$$

$$[OH^-]_{flot} = \frac{0,028mol}{23dm^3} = 0,00122mol/dm^3$$

$$pOH_{flot} = -\log_{10} \frac{0,00122mol}{dm^3} = 2,9145$$

$$pH_{flot} = 14 - 2,9145 = 11,08$$

Appendix IX. Theoretical surfactant amount calculations

Surfactant 4	The mass of ink (g) per ton paper	Density of Ink (g/m ³)	Total volume of the ink (m ³)	Radius on the ink particle sphere (m)	Total volume of the ink spheres (m ³)
0,50 %	5 000	1099407,4706309	0,00454790433353225	1,00E-06	4,18879E-18
0,50 %	5 000	1099407,4706309	0,00454790433353225	5,00E-06	5,23599E-16
0,50 %	5 000	1099407,4706309	0,00454790433353225	1,50E-05	1,41372E-14
2 %	20 000	1099407,4706309	0,018191617334129	1,00E-06	4,18879E-18
2 %	20 000	1099407,4706309	0,018191617334129	5,00E-06	5,23599E-16
2 %	20 000	1099407,4706309	0,018191617334129	1,50E-05	1,41372E-14
Surfactant 8	The mass of ink (g) per ton paper	Density of Ink (g/m ³)	Total volume of the ink (m ³)	Radius on the ink particle sphere (m)	Total volume of the ink spheres (m ³)
0,50 %	5 000	1099407,4706309	0,00454790433353225	1,00E-06	4,18879E-18
0,50 %	5 000	1099407,4706309	0,00454790433353225	5,00E-06	5,23599E-16
0,50 %	5 000	1099407,4706309	0,00454790433353225	1,50E-05	1,41372E-14
2 %	20 000	1099407,4706309	0,018191617334129	1,00E-06	4,18879E-18
2 %	20 000	1099407,4706309	0,018191617334129	5,00E-06	5,23599E-16
2 %	20 000	1099407,4706309	0,018191617334129	1,50E-05	1,41372E-14
Surfactant 9	The mass of ink (g) per ton paper	Density of Ink (g/m ³)	Total volume of the ink (m ³)	Radius on the ink particle sphere (m)	Total volume of the ink spheres (m ³)
0,50 %	5 000	1099407,4706309	0,00454790433353225	1,00E-06	4,18879E-18
0,50 %	5 000	1099407,4706309	0,00454790433353225	5,00E-06	5,23599E-16
0,50 %	5 000	1099407,4706309	0,00454790433353225	1,50E-05	1,41372E-14
2 %	20 000	1099407,4706309	0,018191617334129	1,00E-06	4,18879E-18
2 %	20 000	1099407,4706309	0,018191617334129	5,00E-06	5,23599E-16
2 %	20 000	1099407,4706309	0,018191617334129	1,50E-05	1,41372E-14

Table 27. Theoretical amount of ink calculations, part 1

Number of spheres	Spheres surface area (m ²)	Total area to be covered (m ²)	Area per surfactant molecule (m ²)	Number of surfactant molecules	Molecules / mol
1,08573E+15	1,25664E-11	13 643,7130005968	1,00E-16	1,36437E+20	6,02E+23
8,68586E+12	0,0000000003141592 65358979	2 728,74260011935	1,00E-16	2,72874E+19	6,02E+23
3,21698E+11	0,000000002827433 38823081	909,58086670645	1,00E-16	9,09581E+18	6,02E+23
4,34293E+15	1,25664E-11	54 574,852002387	1,00E-16	5,45749E+20	6,02E+23
3,47434E+13	0,0000000003141592 65358979	10 914,9704004774	1,00E-16	1,0915E+20	6,02E+23
1,28679E+12	0,000000002827433 38823081	3 638,3234668258	1,00E-16	3,63832E+19	6,02E+23
Number of spheres	Spheres surface area (m ²)	Total area to be covered (m ²)	Area per surfactant molecule (m ²)	Number of surfactant molecules	Molecules / mol
1,08573E+15	1,25664E-11	13 643,7130005968	1,00E-16	1,36437E+20	6,02E+23
8,68586E+12	0,0000000003141592 65358979	2 728,74260011935	1,00E-16	2,72874E+19	6,02E+23
3,21698E+11	0,000000002827433 38823081	909,58086670645	1,00E-16	9,09581E+18	6,02E+23
4,34293E+15	1,25664E-11	54 574,852002387	1,00E-16	5,45749E+20	6,02E+23

3.47434E+13	0.0000000003141592 65358979	10914.9704004774	1.00E-16	1.0915E+20	6,02E+23
1.28679E+12	0.000000002827433 38823081	3638.3234668258	1.00E-16	3.63832E+19	6,02E+23
Number of spheres	Spheres surface area (m2)	Total area to be covered (m2)	Area per surfactant molecule (m2)	Number of surfactant molecules	Molecules / mol
1.08573E+15	1.25664E-11	13 643.7130005968	1.00E-16	1.36437E+20	6,02E+23
8.68586E+12	0.0000000003141592 65358979	2728.74260011935	1.00E-16	2.72874E+19	6,02E+23
3.21698E+11	0.000000002827433 38823081	909.58086670645	1.00E-16	9.09581E+18	6,02E+23
4.34293E+15	1.25664E-11	54574.852002387	1.00E-16	5.45749E+20	6,02E+23
3.47434E+13	0.0000000003141592 65358979	10914.9704004774	1.00E-16	1.0915E+20	6,02E+23
1.28679E+12	0.000000002827433 38823081	3638.3234668258	1.00E-16	3.63832E+19	6,02E+23

Table 28. Theoretical amount of ink calculations, part 2

Number of surfactants (mol)	Molecular mass (g/mol)	Mass (g) per ton to cover ink with surfactant
0.000226559137937909	5000	1.13279568968955
0.0000453118275875818	5000	0.226559137937909
0.0000151039425291939	5000	0.0755197126459697
0.000906236551751636	5000	4.53118275875818
0.000181247310350327	5000	0.906236551751636
0.0000604157701167757	5000	0.302078850583879
Number of surfactants (mol)	Molecular mass (g/mol)	Mass (g) per ton to cover ink with surfactant
0.000226559137937909	1750	0.396478491391341
0.0000453118275875818	1750	0.0792956982782681
0.0000151039425291939	1750	0.0264318994260894
0.000906236551751636	1750	1.58591396556536
0.000181247310350327	1750	0.317182793113073
0.0000604157701167757	1750	0.105727597704358
Number of surfactants (mol)	Molecular mass (g/mol)	Mass (g) per ton to cover ink with surfactant
0.000226559137937909	520	0.117810751727713
0.0000453118275875818	520	0.0235621503455425
0.0000151039425291939	520	0.00785405011518084
0.000906236551751636	520	0.471243006910851
0.000181247310350327	520	0.0942486013821701
0.0000604157701167757	520	0.0314162004607234

Table 29. Theoretical amount of ink calculations, part 3

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