Paper chemistry

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Sodium dodecyl sulphate (SDS) residue analysis of foam-formed cellulose-based products

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Abstract: Surfactant residues in foam forming are related to the circulation of surfactant in the foaming process, but they may also affect the properties of the foam-formed product. In this work, residues of an anionic surfactant, sodium dodecyl sulphate (SDS), in foam-formed products were studied. Two different methods were applied for the determination of SDS: ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and solvent extraction spectrophotometry. The dry matter content of the sample before the drying step has a significant effect on the SDS residue. Another factor that has a significant effect on the SDS residues is the amount of precipitated dodecyl sulphate (DS). It was found that SDS does not degrade in the drying phase and will remain in the salt form in the final product. SDS residue decreased when the temperature of the fibre suspension was increased. Theoretical values for SDS residues were estimated from the original surfactant concentration and the amount of water remaining in the product before the drying phase. When all the surfactant was in soluble form, measured SDS residues were close to the theoretical values, which indicates that SDS was not permanently adsorbed onto softwood cellulose fibres.

Keywords: foam forming; ICP-OES; papermaking; sodium dodecyl sulphate; surfactant residues.

Introduction

The concept of foam forming in papermaking was introduced in the beginning of the 1970s (Smith and Punton 1975, Radvan and Gatward 1972, Punton 1975, Smith et al. 1974). In foam forming, fibres are dispersed in aqueous

foam instead of in water. Fibre-foam mixture can be generated using various methods of introducing gas to the liquid (mechanical stirring, bubbling through a porous plate and use of turbulence generators). It is critical that the formation of foam is faster than its breakdown and to achieve this, the presence of a surfactant is required. Furthermore, the surface tension of a solution decreases as the concentration of surfactant increases. This means that less energy is needed to create a new liquid/gas interface. In recent years, several publications related to foam forming have been published (Alimadadi and Uesaka 2016, Hou and Wang 2017, Lappalainen et al. 2014, Al-Qararah et al. 2013, 2015a, 2015b, Lehmonen et al. 2013, Li et al. 2016, Mira et al. 2014, Turpeinen et al. 2018, Wenchao et al. 2018).

The choice of surfactant is important, and the following properties should be considered in addition to good foaming properties:

- The surfactant dosage should be minimised. High surfactant concentrations in wastewater treatment plants (WWTP) result in high chemical oxygen demand (COD) loads. Chemical costs are also lower at low dosage levels.
- The surfactant should be readily biodegradable.
- The toxicity of surfactant towards aquatic organisms and microorganisms should be as low as possible.

Small molecular anionic surfactants such as sodium dodecyl sulphate (SDS) are well suited for foaming of fibre suspensions. SDS (CAS: 151-21-3; MW: 288.38 g/mol) has frequently been used as a foaming aid when studying fibre foams and foam forming (Al-Qararah et al. 2013, 2015a, 2015b, Lappalainen et al. 2014, Lehmonen et al. 2013, Mira et al. 2014, Turpeinen et al. 2018). SDS is also commonly used in detergents, household cleaning products and personal care products. Good foaming properties (rapid foaming, high air content, slow drainage) have been observed with SDS when producing fibre foams from pulp suspensions. Mira et al. (2014) reported that in laboratory-scale studies the minimum surfactant dosage to reach an air content of 66 % for SDS was 0.6 g/l, which was much lower than for many non-ionic surfactants.

Because of their amphiphilic nature, surfactants may be harmful or even toxic to aquatic organisms. Surfac-

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tants can penetrate through tissues (e. g. fish gills) and bind to biomolecules, such as enzymes and phospholipid membranes, causing changes in cellular activity. In general, cationic and non-ionic surfactants are more toxic to aquatic species than anionic surfactants (Ivanković and Hrenović 2010). Therefore, surfactant concentrations in industrial wastewaters must be reduced to the permissible level before discharging into natural waters. Surfactants used in foam forming should be readily biodegradable and must not be toxic to microorganisms that are responsible for the biological treatment of wastewater in WWTP. SDS is relatively hydrophilic (water solubility 100–150 g/l and $\log P_{ow} = 1.6$) and it is readily biodegradable in aerobic conditions. Alkyl sulphates also degrade rapidly in an anaerobic environment, unlike many other common surfactants (Scott and Jones 2000). The reported Predicted No Effect Concentrations (PNEC) for SDS in fresh water and in a sewage treatment plant were 0.137 mg/l and 1 084 mg/l, respectively (Sodium dodecyl sulphate MSDS 2018). Due to these properties, SDS has a low tendency to bioaccumulate and is considered as a substance of low toxicity (IPCS InChem 2019).

There are several different methods for analysing surfactant concentrations in water samples (Schmitt 2001). The ability to determine surfactant residues is essential because their concentrations are directly related to the circulation of surfactant in the process but also because surfactant residues may affect the properties of the foam-formed product, e. g. strength properties (Lappalainen et al. 2014). Other chemicals (wet-strength, dry-strength, fillers) are also used in the process (Vähä-Nissi et al. 2018). Surfactants can have different interactions with these chemicals and, as a result of these interactions, surfactant residues in the product may vary. The high content of surfactants in the foam-formed end product could cause problems, for example, in recycling (unwanted foaming). Surfactant residues are also important from the point of view of product safety. Paper and board which are used as food contact materials must fulfil the requirements set in national and supranational regulations. Regulations assess permitted substances and raw materials in food contact materials and migration limits or limits of residual content for the substances. The migration limit defines the amount of a chemical substance that is permitted to diffuse from a food contact material into food (Ossberger 2015). SDS is mentioned in the list of approved substances in several regulations concerning direct and indirect food additives set by the U.S. Food and Drug Administration (FDA). SDS has approval for use in paper and paperboard which are intended to come into contact with aqueous or fatty foods (e-CFR 2019). According to the German Federal Institute for Risk

Assessment (BfR), SDS can be used as a production aid in paper and paperboard which is used as food contact material (up to 1 %). However, migration of alkyl sulphates from the coating of food contact material must not exceed 500 mg/m² (BfR 2017).

It is well known that surfactants in cleansers may induce skin and eye irritation and damage the barrier function of the skin. In addition to removing dirt, oil and sweat from the skin surface, surfactants in cleansers can interact with the proteins and lipids of the outermost layer of skin. Surfactants may induce, e. g. dryness, redness, cracking and itching on the skin and reddening and tearing of the eyes. In general, anionic surfactants are considered to be more irritating to the skin than non-ionic surfactants because of their ability to bind to proteins (Ananthapadmanabhan et al. 2004, Cassiday 2016, Mehling et al. 2007, Kronberg et al. 2014). A prerequisite for products which are intended to come into contact with skin and eyes is that they need to have a low potential for skin and eye irritation. The irritation potential is highly dependent on the chemical structure of the surfactant, surfactant concentration, and also on pH and the duration of skin contact (Mehling et al. 2007, Seweryn 2018). SDS is relatively irritating to skin and eyes. It has been used as a model surfactant and as a control substance in studies concerning surfactant-induced skin irritation (Kronberg et al. 2014, Lémery et al. 2015, Mehling et al. 2007, Yanase and Hatta 2018).

Surfactant residues in foam-formed products can be estimated at a theoretical level from the water content of the product before drying and the amount of surfactant present in the water (see Figure 1). In this approach, it is

Figure 1: Theoretical estimation of surfactant residues in foam-formed products. The graph shows the dependence of surfactant residues on the surfactant dosage and the dry matter content before drying.

assumed that surfactant is left in the product with water at the same concentration as dosed. It is assumed that there are no chemical interactions that would cause the surfactant to adsorb to the fibre network or reject adsorption. Surfactant is expected to remain in the product when water is evaporated. For example, SDS remains in the final product as a salt when the water evaporates. This requires conditions, in which the water does not leave the product as an aerosol. When the surfactant dosage, the dry matter content (DM) of the sample before drying and the grammage of the absolute dry sample are known, the theoretical amount of surfactant residues can be calculated as follows

$$\begin{aligned} &\text{Surfactant residues (mg/m}^2\text{)} \\ &= \left[\frac{1 - \text{DM}}{\text{DM}} \cdot \text{GSM}_{\text{dry}} \text{ (g/m}^2\text{)} \right] \cdot [\beta \text{ (g/kg)}] \quad (1) \end{aligned}$$

where DM is dry matter content before drying, GSM_{dry} is the grammage of the sample and β is surfactant dosage (grams of surfactant per one kilogram ($\approx$ one litre) of water). The term within the first bracket indicates the amount of water and the term within the second bracket indicates the amount of surfactant in water. DM is calculated as follows

$$\text{DM} = \frac{m_{\text{dry}}}{m_{\text{wet}}} \quad (2)$$

where m_{dry} is the weight of the completely dried sample and m_{wet} is the weight of the wet sample.

In this article, two methods for determination of SDS from foam-formed products are introduced: ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and solvent extraction spectrophotometry. ICP-OES is an analytical technique which is suitable for the determination of trace elements both in solid and liquid samples (Hou and Jones 2000). SDS can be detected by ICP-OES by measuring the sulphur content. Solvent extraction spectrophotometry is based on the detection of surfactant molecules by the formation of a coloured ion pair that can be detected spectrophotometrically in the visible light area (Schmitt 2001). SDS may lose its surface-active properties due to autocatalytic hydrolysis or biodegradation (Bethell et al. 2001, Thomas and White 1989). Because ICP-OES detects the total amount of sulphur, it also detects the sulphur arising from the decomposed SDS. Therefore, ICP-OES cannot differentiate between the surface active SDS molecule and decomposed SDS. On the other hand, the spectrophotometric method detects only the surface active SDS molecule. To carry out the determination, the surfactant must be transferred from the solid sample into

the liquid phase. Before the ICP-OES analysis, the samples were prepared using ultrasound-assisted nitric acid digestion. For the spectrophotometric determination, SDS was extracted from the foam-formed sample with water. To the best of our knowledge, there is currently no other publication concerning the determination of surfactant residues in foam-formed materials.

Materials and methods

Materials

Never dried pre-refined bleached softwood kraft pulp was used in this study. The pulp was obtained from a Finnish pulp mill. The average fibre length of the pulp was 1.96 mm, and the Schopper-Riegler freeness was 18. Calcium chloride hexahydrate $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, purity 98 %) was used to adjust the water hardness of the pulp suspension. Cationic potato starch Raisamyl 70021 (Chemigate Ltd.) was used as a dry strength improvement aid. Sodium dodecyl sulphate (SDS) was used as a surfactant. SDS powder (purity $\geq 90\%$) was purchased from Sigma-Aldrich. The purity of SDS was not taken into account, i.e. concentrations were calculated assuming 100 % purity of the product. Nitric acid (Fluka, purity $\geq 65\%$) was used as received in the ultrasound-assisted digestion.

Preparation of foam-formed samples

The pulp was diluted with deionised water to a consistency of 0.5 % and then blended under mild stirring. The initial water hardness of the fibre suspension was approximately 2 °dH. The conductivity and pH of the suspension were 105 $\mu\text{S/cm}$ and 9.2, respectively. Water hardness was increased by adding CaCl_2 solution so that the final water hardness was 7 °dH. After addition, the conductivity and pH were 303–306 $\mu\text{S/cm}$ and 8.3–8.9, respectively. When cationic starch was used, the pulp was stirred for at least 30 min after the starch addition in order to allow it to bind to the fibres. Cationic starch dosage was 20 kg/t of dry fibres.

The pulp formulation was placed into a transparent vessel ($\varnothing$ 160 mm) and SDS was added. SDS was dosed as 10 % stock solution. The foam was generated using a Netzsch Drill Pulp Agitator using a mixing rate of 3650 rpm. The mixing plate ($\varnothing$ 83 mm) was placed just below the surface of the water-fibre suspension to ensure the most effective mixing. Mixing was continued until the vortex was closed. Foam-formed hand sheets were prepared using a

foam hand sheet mould according to the procedure described earlier (Lappalainen et al. 2014, Mira et al. 2014). Target grammage of the sheets was 100 g/m². When paper sheets were prepared, water was removed by vacuum, and the obtained sheet was couched. The paper sheets were dried in air on a wire overnight. When porous sheets were prepared, water was drained first by the influence of gravitation for 10 min, which resulted in a very bulky and wet structure. The residual water was removed by evaporation in an oven at 70 °C.

Spectrophotometric determination

For the spectrophotometric determination, SDS was extracted from the solid sample using deionised water. Approximately 0.5–1.0 g of sample was weighed and shredded. The sample was disintegrated in approx. 200 ml of deionised water using a hand blender. The mixture was filtered through a paper filter with a pore size of 8 µm (Whatman no. 40) and washed two times with approx. 250 ml of deionised water. Finally, the filtrate was filtered through 0.45 µm mixed cellulose ester membrane filter (Whatman ME 25) by suction, in order to obtain a clear solution that did not contain any fibres or fines. SDS concentration was measured from the filtrate. The spectrophotometric determination of SDS was carried out with a Hach Lange DR3900 VIS spectrophotometer using the Hach Lange LCK cuvette test system. The LCK432 cuvette test for anionic surfactants was used, which is based on the reaction with methylene blue (ISO 7875-1). Anionic surfactant and methylene blue form a complex that is extracted in chloroform. The absorbance of the chloroform phase is measured at 653 nm. Calibration with known concentrations of SDS was performed. The calibration solutions were diluted in deionised water. The same SDS grade was used in the calibration as in the preparation of foam-formed samples. The correlation coefficient of the calibration curve was 0.999.

ICP-OES

Before the analysis, the foam-formed samples were pre-treated using ultrasound-assisted nitric acid digestion. Approximately 0.5 g of the sample was accurately weighed and shredded. The pieces of the sample were placed into a 50 ml plastic screw-top tube and 10 ml of concentrated nitric acid was added. The closed tube was placed into an ultrasonic water bath (Bandelin Sonorex) at approximately 70 °C. The samples were sonicated for 3 x 3 min. After each cycle, screw-tops were opened to relieve the pressure. After

sonication, the samples were filtered through a filter paper with a pore size of 20–25 µm (Whatman no. 41) and diluted to 50 ml volume. A foam-formed hand sheet prepared using Tween 20 as a surfactant served as the blank sample for ICP-OES measurements. The blank sample was used to determine the sulphur content in the pulp. SDS residue was calculated from the measured sulphur content after subtracting the blank value.

A PerkinElmer Optima 8300 DV ICP-OES was used in the determination. The instrument was equipped with a 40 MHz FlatPlate RF generator, a GemCone Low-Flow nebuliser and a cyclonic spray chamber. Sulphur contents of the samples were measured at 180.669 nm using an axial measuring view. The sample introduction system was flushed between every sample with 5% nitric acid. The measurement parameters used in the quantitative measurement are presented in Table 1. Sulphur calibration solutions were prepared from ammonium sulphate (NH₄)₂SO₄ with the nitric acid background. The measurements were carried out using either four- or five-point calibration.

Table 1: Measurement parameters used in ICP-OES for the determination of sulphur.

Measurement parameters	
RF power	1500 W
Outer argon flow	8 l/min
Intermediate argon flow	0.2 l/min
Inner argon flow	0.6 l/min
Sample flow rate	1.50 ml/min
Measuring view	Axial

Water hardness measurement

Water hardness is caused by calcium and magnesium cations in water. Water hardness was measured with a Hach Lange DR3900 VIS spectrophotometer using the calmagite colorimetric method. The measurement is based on the colour changes of the indicator dye calmagite, which forms a purplish-blue colour in a strongly alkaline solution and changes to red when it reacts with free calcium or magnesium. Calcium and magnesium determinations are made by chelation of calcium with EGTA to remove the red colour from calcium and then chelation of calcium and magnesium with EDTA to remove the red colour from both calcium and magnesium. The measurement of the red

colour in the different states is used to measure the calcium and magnesium concentrations. The measurement wavelength in the method is 522 nm. The results were converted to units of the German degree of hardness (°dH). According to the definition of the German degree of hardness, 1 °dH corresponds to 10 mg/l of calcium oxide (CaO).

Turbidity measurement

A turbidity meter evaluates the degree of scattered light, which indicates the amount of insoluble particles present in solution. Turbidity of SDS water solutions was measured at several different temperatures. SDS solutions of several different concentrations below and above the critical micelle concentration (CMC) were prepared in tap water. The samples were prepared at least an hour before the measurements in order to ensure precipitation of the salts, and were stirred carefully during this time. The samples were kept at the desired temperature in a water bath for at least 15 min before the measurements. Turbidity measurement was carried out with a Hach 2100AN IS Laboratory Turbidimeter. The optical system in the turbidimeter includes an 870 ± 30 nm light emitting diode (LED) assembly, a 90° detector to monitor scattered light, a forward-scatter light detector, a transmitted-light detector and a back-scatter light detector. The complete set of detectors ("Ratio" mode) was used in the measurement.

Results and discussion

Determination of SDS using ICP-OES and spectrophotometry

Handmade foam-formed paper sheets and porous sheets were prepared to compare the two different determination methods for SDS: ICP-OES and the spectrophotometric determination. The sheets were prepared using different dosages of SDS: 0.4, 0.6, 1.2, 1.8 and 2.4 g/l. Water hardness varies in different locations. There may also be variation depending on the season and water consumption. For example, the hardness of tap water in Jyväskylä at VTT varies between 2.2 and 4 °dH, depending on which waterworks the tap water comes from. The water hardness of 0.5 % pre-refined pine pulp diluted in deionised water was approximately 2 °dH. To determine the effect of water hardness, another pulp sample was prepared by adding CaCl_2 . The water hardness of the pulp was 7 °dH after calcium addition.

Figure 2: The measured SDS residue as a function of SDS dosage in the air-dried foam-formed paper sheets. Water hardness of the pulp was adjusted to 7 °dH. The theoretical points were calculated from the DM of the wet sheets before drying, which was approximately 23.5 %. Some of the data points are the average values of replicate samples.

Figure 3: The measured SDS residue as a function of SDS dosage in the fibrous porous sheets. Water hardness of the pulp was adjusted to 7 °dH. The porous sheets were very wet before drying. The theoretical points were calculated from the DM of the wet sheets before drying which was approximately 5.2 %. The error bars in the theoretical points were calculated by assuming $\pm 1\%$ -unit deviation in the DM before drying.

SDS residues in the samples were determined by ICP-OES and spectrophotometry. Figures 2 and 3 present the measured SDS residue as a function of SDS dosage in the air-dried paper sheets and the porous sheets, respectively. The graphs also show the corresponding theoretical

cal residues calculated by equation 1. To calculate the theoretical values, dry matter content (DM) of the wet hand sheet was determined before drying. The DM before drying was approximately 23.5% for the paper sheets and 5.2% for porous sheets. The deviation in the DM before drying was higher in the case of porous sheets, and therefore, error bars in theoretical points of Figure 3 were calculated by assuming 1%-unit deviation in the DM before drying.

ICP-OES and spectrophotometric determination gave very similar results. This indicates that SDS can be extracted from a foam-formed sample with water and that the spectrophotometric determination method for SDS is also suitable for solid fibre samples. As the spectrophotometric determination method is based on the detection of non-degraded SDS molecules, it can be concluded that SDS did not degrade during the drying phase, i. e. it remained surface active. SDS residue increased as the SDS dosage increased. As shown in Figure 2, the measured SDS residues were close to the theoretical values at low SDS dosages (≤ 0.6 g/l). However, at higher SDS dosages the measured SDS residues were much higher than the corresponding theoretical values.

By comparing Figures 2 and 3 it can be seen that SDS residues were significantly higher in porous sheets than in thin paper sheets. The maximum measured SDS residue in the paper sheets was about 22.5 mg/g (see Figure 2). Figure 3 shows that the lowest measured SDS residues in the porous sheets were above this value. The amount of water and therefore the amount of SDS was greater in the porous sheets. In the porous sheets, the measured SDS residues were also much higher than the theoretical values at every SDS dosage level (also at 0.4 g/l). It is interesting to note that a decrease in measured SDS residue was observed at the SDS dosage of 2.4 g/l which is slightly above the critical micelle concentration (CMC) of SDS. At the SDS dosage of 0.6 g/l, more SDS was found from the porous sheets (41–49 mg/g) compared to the paper sheets (2.2–2.3 mg/g). Thus, at that dose the porous sheets contained about 20 times the amount of the SDS compared to thin sheets.

The differences between thin and porous samples are due to two reasons. The first reason is obvious, i. e. the differences in the DM before drying. The amount of water in the porous sheets was approximately 5-fold compared to the paper sheets. The second reason is related to the precipitation of dodecyl sulphate (DS). The precipitate can attach to the fibre network during drainage. When generating foam, high shear forces in the mixing can prevent or at least reduce the precipitation. When making paper sheets, the foam is collapsed quickly by vacuum, so the dewatering time is short, whereas in the case of porous

Figure 4: Measured SDS residue in the foam-formed samples as a function of the calculated theoretical SDS residue. Results for the SDS dosage of up to 1.8 g/L are shown. The measured residues are approximately three times higher than the theoretical residues. The correlation coefficient of the linear curve is $R^2 = 0.97$.

sheets the water is removed by gravity and the dewatering time is much longer. Precipitation of dodecyl sulphate salts requires time, and therefore there are more precipitated DS salts in the porous samples compared to thin paper samples. For the above two reasons, the measured SDS residues were much higher in the porous sheets than in the thin sheets.

Figure 4 presents the measured SDS residues in the air-dried paper sheets and the oven-dried porous sheets as a function of theoretical SDS residues up to an SDS dosage of 1.8 g/l. It can be seen from the plotted curve that the dependence between the measured and the theoretical SDS residue is linear ($R^2 = 0.97$). The slope of the curve tells that the measured SDS residues were about threefold that of the theoretical ones. The highest measured value was close to 100 mg/g (see Figure 4). Therefore, if one gram of the sample was disintegrated in one litre of water, the SDS concentration of the suspension would be about 100 mg/l. In practice, such a suspension can be foamed without adding more surfactant.

The effect of water hardness, temperature and cationic starch

It is well known that alkyl sulphates precipitate as salts with divalent and trivalent cations, such as calcium, magnesium, barium and iron (Milton 2004, Miyamoto 1960, Schmitt 2001). Anionic SDS may also interact with cationic additives. Turpeinen et al. (2018) reported that agglomerates were formed in foam-formed porous fibre samples

due to the use of cationic starch and SDS together. Therefore, we wanted to investigate the effect of water hardness and temperature of the pulp as well as of the addition of cationic starch on SDS residues. Air-dried paper sheets were prepared in the following conditions: 1) water hardness 7 °dH and room temperature (22 °C), 2) water hardness 2 °dH and room temperature, 3) water hardness 7 °dH and 50 °C and 4) water hardness 2 °dH, room temperature, cationic starch addition 20 kg/t of dry fibres. SDS residues in the paper sheets were measured by the spectrophotometric determination method. The DM of the samples (before drying) varied between 19.5 and 23.0 % (see Table 2). Due to the surfactant, the surface tension of water was lower than without the addition of surfactant. As a consequence, the capillary pressure between fibres should be smaller, and dewatering should be easier. In Figure 5, maximum and minimum values for the theoretical SDS residue are shown based on the variation in DM before drying.

Table 2: The measured dry matter contents (DM) before drying of the foam-formed sheets in different preparation conditions.

Preparation conditions	DM before drying (%)
Water hardness 7 °dH, $T = 22\text{ °C}$	21.0–21.8
Water hardness 2 °dH, $T = 22\text{ °C}$	19.5–20.2
Water hardness 7 °dH, $T = 50\text{ °C}$	20.4–23.0
Water hardness 2 °dH, $T = 22\text{ °C}$	21.3–22.3
+ addition of cationic starch 20 kg/t of dry fibres	

Looking at Figure 5, it is apparent that SDS residue increased as the water hardness increased. When water hardness was 7 °dH, SDS residues were higher than the theoretical values. These results are in accordance with the previous measurements from samples made in the same conditions (see Figure 2). When water hardness was 2 °dH, SDS residues decreased close to the theoretical level. SDS residues also decreased when the temperature increased from room temperature to 50 °C while keeping the water hardness level at 7 °dH.

The highest SDS residues were measured in conditions in which water hardness was 7 °dH, the temperature was 22 °C, and cationic starch was used. The measured SDS residue was higher with the use of cationic starch than without starch addition, which would suggest that SDS is adsorbed via ion-ion interactions with cationic starch. However, it should be noted that the dosage of cationic starch was high, 20 kg/t of dry fibre. When using lower dosages of cationic starch, the effect on SDS residue is probably lower. The results indicate that SDS can interact

Figure 5: The effect of water hardness, temperature of the water-fibre suspension and addition of cationic starch on SDS residue. The measured SDS residues are shown in units of mg/g and mg/m². The grammage of the (dried) samples was 100 g/m². The graphs also show the calculated theoretical range for SDS residues. The DM of the samples (before drying) varied between 19.5 and 23.0 %. The curve of maximum theoretical values (Theoretical max.) was calculated using a DM of 19.5 % and the curve of minimum theoretical values (Theoretical min.) using a DM of 23.0 %.

with cationic papermaking additives and in this way accumulate in the fibre structure.

Precipitation of dodecyl sulphate as $\text{Ca}(\text{DS})_2$ and $\text{Mg}(\text{DS})_2$

Calcium and magnesium salts of dodecyl sulphate are weakly soluble, and hence precipitate out from an aqueous solution, which is seen visually as increasing turbidity of the solution. Figure 6 shows a microscopy picture from precipitated calcium dodecyl sulphate $\text{Ca}(\text{DS})_2$ salt crystals in aqueous solution. Here we focus on calcium dodecyl sulphate $\text{Ca}(\text{DS})_2$ because it is much less soluble than magnesium dodecyl sulphate $\text{Mg}(\text{DS})_2$ (Goddard 1975, Miyamoto 1960). The solubility of $\text{Ca}(\text{DS})_2$ increases with increasing temperature and is only 0.46 mM (0.26 g/l) at 25 °C. In comparison, the solubility of SDS at 20 °C is 451 mM (130 g/l). The Krafft temperature (i. e. the temperature at which the solubility of a surfactant increases strongly) of $\text{Ca}(\text{DS})_2$ is 50 °C at which the solubility is 1.62 mM (0.92 g/l), and at 52 °C the solubility is 2.09 mM (1.66 g/l) (Miyamoto 1960).

Figure 6: An optical microscopy picture of an aqueous SDS solution with an SDS concentration of 1.7 g/l and water hardness 10 °dH. The scale bar is 50 μm.

According to the precipitation phase boundary curves in the literature, hardness tolerance of SDS decreases as SDS concentration increases until it reaches the CMC. When SDS is added into an aqueous solution containing 1 mM of Ca^{2+} ions at 30 °C, dodecyl sulphate starts to precipitate with calcium when the concentration of SDS exceeds 1 mM (0.29 g/l) (Stellner and Scamehorn 1989). In this study, water hardness was adjusted to 7 °dH, so there were 1.2 mM Ca^{2+} ions in the suspension. SDS dosages varied from 0.4 to 2.4 g/l. Thus, in all the conditions where room temperature was applied, a part of dodecyl sulphate was precipitated as $\text{Ca}(\text{DS})_2$. The precipitated $\text{Ca}(\text{DS})_2$ salt remained in the fibre network, which explains the increase in the measured SDS residue. During the drainage, the fibres act as a barrier in which $\text{Ca}(\text{DS})_2$ salt is retained. However, one should notice that the precipitation of dodecyl sulphate requires time. In the studies of solubility, the equilibration times have been from 10 h to several days (Miyamoto 1960, Stellner and Scamehorn 1989). In Figure 2, it was shown that SDS residue was at the theoretical level at the SDS dosage of 0.4 g/l. It is probable that no precipitated $\text{Ca}(\text{DS})_2$ was formed at the lower SDS dosages because the interaction time with calcium ions in the aqueous solution was short, only approximately 2 min. Also, the high shear forces in the mixing prevent partly the formation of $\text{Ca}(\text{DS})_2$ precipitate. When the dewatering phase was longer (10 min), SDS residues also increased at the lower SDS dosages.

Turbidity measurement can be used as a tool to evaluate the amount of precipitated $\text{Ca}(\text{DS})_2$ and $\text{Mg}(\text{DS})_2$ salts in the solution. Figure 7 shows turbidity values (as Neph-

Figure 7: Turbidity of SDS solutions at different temperatures. The samples were prepared in tap water with a hardness of 4.1 °dH.

elometric Turbidity Units, NTU) of SDS solutions at several different concentrations and temperatures. The SDS solutions were prepared in tap water. The hardness of the tap water was 4.1 °dH. As seen in Figure 7, turbidity was highest at room temperature (22 °C) and close to the CMC of SDS (2.4 g/l). The turbidity and hence the amount of precipitated $\text{Ca}(\text{DS})_2$ and $\text{Mg}(\text{DS})_2$ salts decreased steadily when the temperature increased. At 50 °C (which is the Krafft point of $\text{Ca}(\text{DS})_2$) there were no precipitated salts in any of the samples. It has been shown that the hardness tolerance of SDS is better at SDS concentrations above the CMC (Stellner and Scamehorn 1989). Turbidity measurements showed that the amount of precipitated $\text{Ca}(\text{DS})_2$ and $\text{Mg}(\text{DS})_2$ decreased when SDS concentration was increased above the CMC. Above the CMC, the solution contained surfactant molecules as free monomers and micelles. When there are micelles in solution, free Ca^{2+} and Mg^{2+} ions are also bound onto the surface of micelles. As a result, the amount of free Ca^{2+} and Mg^{2+} ions in the solution decreases, and in order to achieve chemical equilibrium, dissolution of precipitated salts (such as $\text{Ca}(\text{DS})_2$) increases.

In the porous sheets, a drop in SDS residue was observed when the SDS dosage was close to the CMC (see Figure 3). This is in agreement with the turbidity measurements, in which the amount of precipitated calcium and magnesium salts were observed to decrease at the CMC of SDS.

In the conditions in which dodecyl sulphate was not precipitated out from the solution (due to water hardness)

or when cationic starch was not added, SDS residues in foam-formed sheets appeared to follow the theoretical estimation. This would indicate that there is no chemical adsorption between SDS and softwood kraft fibres. Instead, the temperature of the pulp, water hardness, electrolyte concentration and the presence of papermaking chemicals with cationic charge may have an effect on SDS residues in foam-formed products.

According to the Recommendation XIV on Polymer Dispersions given by BfR, migration of alkyl sulphates from the coating of food contact material must not exceed 500 mg/m^2 (BfR 2017b). This limit is only a limit of migration into food, not a limit of SDS residue. However, if SDS residue is below 500 mg/m^2 , exceeding the migration limit is theoretically impossible. Figure 5 shows that the measured SDS residues in the paper sheets were below this level in all the tested preparation conditions when using SDS dosage of 0.4 g/l . It is worthy of note that SDS concentrations of process waters in pilot scale generally vary between 0.02 and 0.3 g/l (Koponen et al. 2018). However, when using cationic starch, the residue level of 500 mg/m^2 was exceeded at the SDS dosage of 0.6 g/l . Figure 5 also shows that when the water hardness was low (2 dH°) or the temperature of the suspension was high (50°C), SDS residues were below 500 mg/m^2 or only slightly above it up to an SDS dosage of 1.2 g/l . The results indicate that when the precipitation of dodecyl sulphate with divalent salts can be restrained, it is also possible to use higher SDS dosages without the SDS residue exceeding 500 mg/m^2 .

Conclusions

SDS residues were measured from cellulose-based foam-formed paper sheets and porous sheets. The samples were analysed with two measurement methods, first to ensure the reliability of the measurement results, and secondly to detect whether the dodecyl sulphate (DS) molecules are still surface active or are they cleaved into two or more fragments (cleavage of the S-O bond of DS). The two measurement methods were ICP-OES and solvent extraction spectrophotometry. The ICP-OES method was used to determine the amount of sulphur present in the sample and by using solvent extraction spectrophotometry, the amount of DS was determined. Before ICP-OES analysis the foam-formed samples were prepared using ultrasound-assisted nitric acid digestion. For the spectrophotometric determination, SDS was extracted from the foam-formed sample with water. The two methods gave very similar results, which indicates that SDS is not permanently adsorbed on

fibres (it can easily be extracted from the fibre network with water) and is not degraded during the drying phase of the product.

At the same SDS dosage, surfactant residues were significantly higher in porous samples than in thin samples. The differences between thin and porous samples are due to two reasons. The first reason is obvious, i. e. the differences in the DM before drying. As SDS is dissolved in water, SDS residue increases as the amount of water removed by evaporation increases. The second reason is related to the precipitation of dodecyl sulphate. The precipitate can attach to the fibre network during drainage. When generating foam, high shear forces in the mixing can prevent or at least reduce the precipitation. When making thin samples by removing water by vacuum, the dewatering time is short. In contrast, in the case of porous sheets the water is removed by gravity and the dewatering time is much longer. Precipitation of dodecyl sulphate (DS) salts requires time, and therefore there are more precipitated DS salts in the porous samples compared to thin paper samples. For the above reasons, the measured SDS residues are much higher in the porous sheets than in the thin sheets.

Our study showed that SDS residue increased as water hardness increased due to precipitation of dodecyl sulphate as calcium dodecyl sulphate $\text{Ca}(\text{DS})_2$ and magnesium dodecyl sulphate $\text{Mg}(\text{DS})_2$ salts, which remained in the fibre network. When water hardness was adjusted to 7°dH by adding calcium into the pulp, the measured SDS residues in the foam-formed samples were approximately threefold higher than the theoretical SDS residues. Turbidity measurements of SDS water solutions showed that the amount of precipitated $\text{Ca}(\text{DS})_2$ and $\text{Mg}(\text{DS})_2$ depends on the SDS concentration and the temperature of the solution. SDS residues decreased when water hardness of the water-fibre suspension was decreased to 2°dH or when the suspension was heated to 50°C (which is the Krafft point of $\text{Ca}(\text{DS})_2$) before foaming. In these conditions, the measured SDS residues were close to the theoretical values, which indicates that SDS is not permanently adsorbed onto cellulose fibres.

Increase in SDS residues was observed when cationic starch was added. This is due to the electrostatic interactions between the cationic starch and anionic SDS. However, it should be noted that the dosage of cationic starch was high, 20 kg/t of dry fibres. We assume that SDS also interacts with other cationic papermaking additives, resulting in increased SDS residues.

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