CELLULOSE CHEMISTRY AND TECHNOLOGY

ADSORPTION KINETICS OF CATIONIC SURFACTANT ONTO PULP FIBRES

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Received March 26, 2013

Adsorption of cationic compounds on cellulosic fibres totally changed their surface chemistry. The paper is focused on the modification of pulp fibres by a cationic surfactant (quaternary ammonium salts). The work deals with surfactant adsorption kinetics and modes of surfactant adsorption on the cellulosic fibre surface. It was found that the adsorption curve had a rising character. The results showed that the surfactant was not adsorbed onto the fibre surface in monolayer. It can be assumed that the surfactant was also adsorbed into the internal porous structure of the fibres. To monitor the surfactant adsorption on fibres, the method of streaming potential with polyelectrolyte titration was used.

Keywords: pulp fibres, cationic surfactant, adsorption, electrokinetic properties

INTRODUCTION

The adsorption of cationic substances on the solid (pulp fibre surface) – liquid interface has been the subject of many investigations.[1–5] The reason is that the process of adsorption, as well as the kinetics of cationic substances deposition on the cellulosic surface, has not been completely explained so far. There is a great heterogeneity of pulp fibre surfaces depending on the pulping process and the heterogeneity of surfactants applied to the pulp slurry, during papermaking, recycling and deinking.[6] The surface active agents change the surface properties of fibres and influence the papermaking and deinking processes on a large scale. Different surfactants are often used to achieve the required properties of produced fibres, as well as to increase the efficiency of processing steps. Surfactants are surface active agents that change the reaction conditions on the interface already at low concentrations.[6] The adsorption of surfactants onto a cellulose surface is a complex process and is not yet clearly defined. Buschle-Diller *et al.*[7] investigated the effect of chemical modification on the physico-chemical properties of pure cellulose fibres and fibres with non-cellulosic impurities. In the case of pure cellulose fibres, the increasing negative potential indicated the dissociation of most acidic functional groups. On the other hand, if non-cellulosic impurities were present, the plateau was approached by decreasing potential values. This phenomenon shows the additional contribution of dissociating basic groups, for instance lignin phenolic groups, as well as the adsorption of protons on ether and acetal linkages.

The adsorption of different non-ionic surfactants is described as a two-step process.[8-10] The first step is diffusion of surfactant from the bulk solution to a subsurface. The second stage is transport from the subsurface to the surface and subsequent adsorption.

In recent years, considerable attention has been devoted to observe the mechanism and kinetics of cationic surface active agent adsorption to cellulose fibres.[1,2,10,11] As cationic surfactant, CTAB (hexadecyltrimethylammonium bromide) was usually used. Biswas and Chattoraj[10] studied the adsorption of cationic surfactants on the silica-water interface at different bulk concentrations, pH, ionic strengths, temperatures and electrolyte contents. They found that the adsorption follows a two-step first-order rate process with two different process rate constants.

Stana-Kleinischek *et al.*[12,13] investigated the reactivity and electrokinetical properties of different types of regenerated cellulose fibres. They modified the surface of fibers by cationic surfactant. The zeta potential of fibres increases from negative to positive charge with increasing surfactant concentration.

Fava *et al.*[14] and Meader *et al.*[15] studied the adsorption of an anionic surfactant on cotton by the radiotracer method. Fava and Eyring[14] have found that the kinetics of the adsorption of an anionic surfactant on a cotton surface cannot be described by the first-order rate equation. Paria *et al.*[2] devoted their work to the adsorption kinetics of anionic, cationic, and non-ionic surfactants on cellulose fibres. They declared that the kinetics of adsorption is regulated by the first-order nonlinear differential equation. The surfactant molecules can be fixed on the fibre surface depending on their size, but the diffusion into the pores of the cell wall could also occur. Cellulose fibre swells when immersed into water. Swelling of fibre makes its structure open and become more accessible for various modification agents. The swelling process of kraft fibres can affect the adsorption of surfactant molecules onto the surface structure of cellulose fibres. The area of the surface and pores accessible for adsorption will be important.

Stone and Scallan[16] used the solute extrusion method for determining the pore size and their results indicated pore widths of at least 2-20 nm in the case of sulphite and kraft pulps. Because of an effect called "excluded volume", it can be expected that the physical dimensions of the pore spaces measured in this way are about two times larger than the physical diameter of probe molecules.[17] Alince[18] followed the pore size of swelled delignified cell walls by adsorption of polyelectrolytes. He found out that the pore size is rather uniform with an average radius around 100 nm in diameter. Based on adsorption of dextran molecules and polyelectrolytes on fibres, it was concluded that the adsorption also occurred on the pore surface of the cell wall.[16,17] Dimensionally, these pores must be suitable for the particular size of the adsorbed molecules. Even if fibre drying changes its supramolecular structure, the water retention value (WRV), pore size distribution and accessible surface area are preserved.[19,20]

It is assumed that the surfactant adsorption takes place by creating a monolayer or more layers of surfactant on the surface of fibres. The mode of adsorption depends on the charge and molecular weight of the surfactant. The surfactants with low molecular weight can be deposited to the pulp surface in multiple layers.[6]

The aim of this paper is to clarify the process and effect of cationic surfactant adsorption on pulp fibres. Another objective of the paper is to understand where the surfactant is located after adsorption, whether it is adsorbed only on the surface or also in the pores of the swelled pulp fibres.

EXPERIMENTAL

Fibre sample

Bleached unrefined hardwood kraft pulp (Mondi SCP) in a dried state was used. Pulp was prepared from a delignified mix of tree species: beech (80%), maple, ash, hornbeam, birch, oak, and acacia. The fibre sample was disintegrated in deionized water, swollen for 10 minutes and used for polyelectrolyte titration and chemical modification.

Surface active agent

As a modification agent, a cationic surfactant was used. The cationic surface active agent, imidazole derivative of substituted amide of oleic acid, was obtained from Chemotex Děčín a.s., Czech Republic. The molecular weight was 465.7 g mol^{-1}. The added amount of surfactant was from 0.05% up to 50% at the weight of oven dried fibre to observe surfactant adsorption.

Kinetics of cationic surfactant adsorption

For modification the 0.64 g bone dry (b.d.) fibres were suspended in 200 ml of deionized water (pH value 5.4) and swollen for 10 min. Under constant stirring at 800 rpm (magnetic stirrer), a certain amount of cationic surfactant was added (9.38; 21.88 and 43.75 mg/g of bone dry pulp). The pH was determined at 5.0 to 5.5. At different time intervals (0, 0.5, 1, 2, 3, 5, 10, 20 and 30 min), 10 ml of a supernatant was withdrawn by a pipette through a screen with 150-200 mesh for elimination of pulp fibres. The kinetics of cationic surfactant adsorption was analysed in 10 ml of supernatant by polyelectrolyte titration using PCD 02 equipment.

Determination adsorbed surfactant amount

An increasing concentration of cationic surfactant was used to modify the pulp fibres. The amount of non-adsorbed surfactant in the supernatant was determined by titration with Pes-Na. The adsorbed amount of surfactant onto the pulp fibres was calculated as the difference between the amounts of added and non-adsorbed cationic surfactant. The same method was used in the work of Besra *et al.*[21-23] to study surfactant adsorption onto clay surface.

Specific charge density of modified pulp fibres

The specific charge density q of pulp fibres (μeq g^{-1}) was determined from the direct polyelectrolyte titration of modified pulp fibres in PCD equipment to the isoelectric point.

The suspension of fibres (0.64 g b.d. pulp fibres in 200 ml) was prepared with the addition of a certain amount of surfactant under constant stirring at 800 rpm with a magnetic stirrer. After 30 minutes, the pulp fibres were filtrated and washed with 120 ml deionised water 3 times. Then, the fibres were diluted in 200 ml of deionised water and 10 ml of suspension was taken to the PCD measuring cell and titrated with standard polyelectrolyte. The specific charge density can be calculated from the equation:

$$q = f_c\, n\, V\, w^{-1} \qquad (1)$$

where f_c is the conversion factor for the unit of charge density (in this case 1000), n is the concentration of standard polyelectrolyte (mol l^{-1}), V is the volume of added standard polyelectrolyte, w is the weight of fibres in 10 ml of sample.

For PDC measurements (equipment supplied by BTG Instruments GmbH), 0.01 mol/l sodium polyethylensulphonate (PES-Na) was used as a standard anionic polyelectrolyte, and 0.01 mol/l poly-diallyl-dimethyl-ammonium chloride (p-DADMAC) was used as a standard cationic polyelectrolyte, both with their charge density dependent only slightly on pH. The specific surface charge density values reported are the average of five measurements.

Spectrophotometric determination of critical micelle concentration

The UV-VIS spectroscopy was used to determine the critical micelle concentration (cmc) of the used cationic surfactant. UV-VIS diffuse reflectance spectra were measured at room temperature by using a CECIL CE 3055 spectrophotometer. The basic solution was prepared by dissolving 3 g of cationic surfactant in 1 L of deionized water. Samples of different concentration were made by dilution of the basic suspension and were used to determine the pH, which was performed with a Jenway 3510 pH meter.

RESULTS AND DISCUSSION

Cellulose fibres are negatively charged in a neutral aqueous medium. Surfactant adsorption onto fibre surface leads to changes in the specific charge density of pulp fibres (Figure 1). The specific charge density of unmodified unbeaten kraft fibres was determined to be 4.5 μeq g^{-1} by direct polyelectrolyte titration of pulp fibres on PCD 02.

As shown in Fig. 1, the surface charge of fibres changes from a negative to a positive value with an increasing amount of added surfactant. The adsorbed amount of surfactant, at which the isoelectric point[24] of fibres was achieved, corresponds to 1.5 mg g^{-1} b.d. fibres. A further addition of cationic surfactant causes an increase of positive surface charge to a maximum value of 4.4 μeq g^{-1} with the addition of 150 mg surfactant per 1 g b.d. fibre. Some studies have indicated a decrease in the rate of the zeta potential of cellulose fibres by addition of cationic polyelectrolyte. The change is most rapid when the polyelectrolyte has a relatively low molecular mass.[25,26] The same trend can be observed in the case of surface modification by surfactant, as presented in Fig. 1.

In Fig. 2, the time evolution of deposition of cationic surfactant on cellulose fibres for different addition of surfactant is shown. From the kinetic curves, it is obvious that the deposition of surfactant onto the pulp surface is a quite fast process. The rate constants increase with an increasing amount of the added surfactant and are 0.522 s^{-1}, 1.167 s^{-1} and 2.112 s^{-1}. The increasing amount of surfactant does not result in reaching the surface maximal adsorption. The kinetics of adsorption could be rationalized well by the two-site adsorption mechanism.[1,2] It is experimentally proved that the surface of cellulose fibres contain two types of functional groups, namely hydrophilic and hydrophobic ones.[2] The hydrophilic groups furnish the surface negative charge and the cationic surfactant is attracted and adsorbed to such sites.[1,2] The addition of cationic surfactant to the suspension of cellulose fibres leads to the immediate interaction of the fibre surface with surfactant molecules. The shape of the curves in Fig. 2 is the same. At the beginning, a non-linear increase could be observed, followed by a clear stabilization (approximately after 5 minutes). There is a linear relation between the amount of added surfactant (9.38; 21.88 and 43.75 mg/g b.d. fibres) and the amount of maximum adsorbed surfactant (9.38, 20.6 and 38.7 mg g^{-1} b.d. fibres). In their work, Paria *et al.*[2] observed similar adsorption kinetics of a cationic surfactant (CTAB) on filter paper. They declared that the kinetics of adsorption was governed by the first-order non-linear differential equation. However, in this work, only 9.38 and 21.88 mg/g of b.d. fibres were added. For higher addition (43.75 mg/g b.d. fibres), the measured data are best fitted by the third-order non-linear differential equation. The structure of the adsorbed surfactant layer and the way in which it modifies the surface properties depend on the nature of the surfactant and its interaction with the surface (whether due to electrostatic attractions, hydrogen or covalent bonding, or hydrophobic forces).

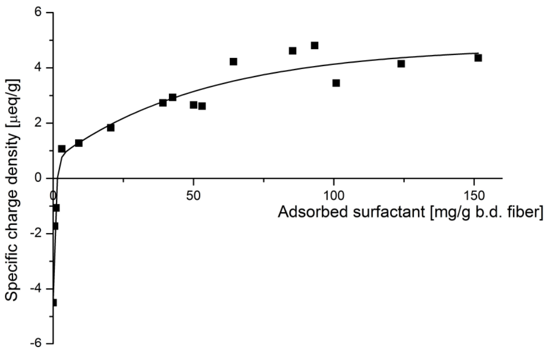

Figure 1: Specific charge density of fibres as a function of adsorbed cationic surface active agent

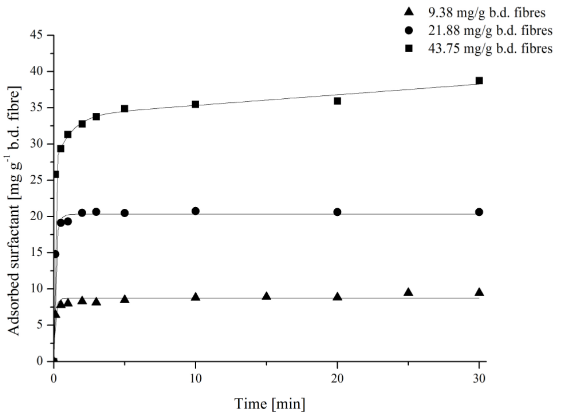

Figure 2: Deposition of cationic surfactant on pulp fibres for different surfactant concentrations

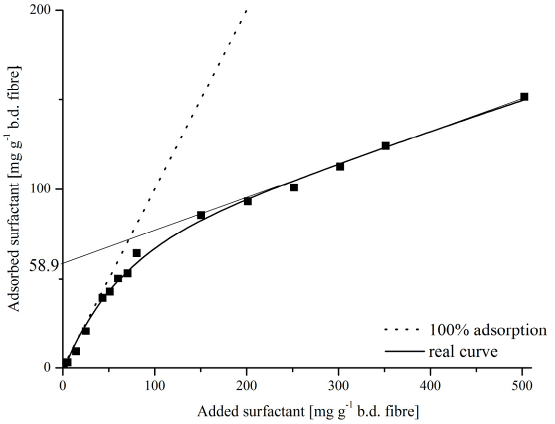

Figure 3: Cationic surfactant adsorption on cellulose fibres after 10 min of equalization

Stemming from theoretical predictions, the amount of adsorbed surfactant should increase with an increasing amount of added surfactant, until reaching equilibrium, when the fibres are unable to embrace a greater amount of surfactant.[27] At the equilibrium point, the fibre surface will be fully covered by surfactant. It is important to know the surface charge density. Its typical value for refined bleached hardwood kraft ranges from 30 to 100 μeq per gram of dry fibre.[28,29] In the case of unrefined bleached hardwood kraft, the surface charge density of 6.3 μeq per gram of b.d. fibres was estimated.

Figure 3 shows the adsorption curves upon addition of cationic surfactant. The adsorption isotherm has two distinct parts. A vertical line represents complete adsorption at low addition level (up to 35 mg g^{-1} fibres surfactant addition). Therefore, there was no surfactant left in the solution.

For surfactant addition of up to 150 mg g^{-1} fibres, a break appears on the curve, and by further addition of cationic surfactant another slower linear increase is observed. This finding corresponds with the results achieved by Penfold *et al.*[1] The equilibrium was not reached in the observed range of added surfactant.

The linear character of the curve in the range of added surfactant from 0.001 to 35 mg g^{-1} fibres leads to the conclusion that the adsorption takes place in the form of a monolayer. The ion exchange capacity of the adsorbed surfactant was estimated at 58.9 mg g^{-1}, which indicates the full saturation of the fibre outer surface by molecules of surfactant.[30] On these assumptions, the amount of adsorbed surfactant deposited in a monolayer on the surface of the fibres and the theoretical quantity of molecules in the aggregate were calculated.

The diameter of surfactant aggregates in an aqueous medium was found to be around 80 nm. The surface area of fibres was approx. 1 m^2 g^{-1}.[31] The total area of fully swollen fiber was approx. 100 m^2 g^{-1}.[32] The weight of surfactant aggregate was calculated for a cubic arrangement on the fibre surface (approx. 1 m^2 g^{-1}) as $4.9 \cdot 10^{-16}$ g, consisting of $6.3 \cdot 10^5$ molecules with an average molecular weight of 465.7 g mol^{-1}.

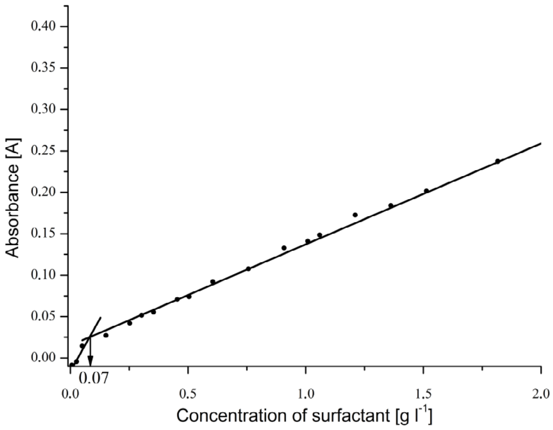

Figure 4: Dependence of absorbance of cationic surfactant solution on the concentration of solution measured at wavelength λ = 316 nm

As we mentioned before, the adsorption increases with increasing addition of surfactant and does not reach the equilibrium. This phenomenon can be explained in several ways. The absorption curve consists in a multilayer adsorption of surfactant on the surface of cellulose fibres. It is assumed that the adsorption of surfactants on solid surfaces takes place in several steps, depending on the amount of added surfactant or its concentration. At a lower amount, all added surfactant is adsorbed and the solid surface is completely covered. With the increasing addition of surfactant, a second monolayer structure, superimposed on the first one, is generated.[5] Above the critical micelle concentration (cmc), cylindrical or spherical aggregates could be formed on the surface. This mechanism is described in the work of Penfold *et al.*[1] The critical micelle concentration was estimated by the UV-VIS spectrophotometry. Pure deionised water was chosen as background. UV-VIS pseudo-absorbance of the samples showed a maximum at λ = 316 nm.

The dependence of absorbance on the concentration of surfactant is shown graphically in Fig. 4. The curve was obtained by reading the value of absorbance at a wavelength λ = 316 nm for each measured concentration. The dependence of absorbance (A) on the concentration of the sample is described by Lambert-Beer's law:

$$A_k = \varepsilon_\lambda \, l \, c \qquad (2)$$

where ε_λ is the molar absorption coefficient, parameter l represents the distance passed by the beam through the measured substance.

Lambert-Beer's law dictates the linear absorbance/concentration dependence. If the critical micelle concentration is reached, at which the surfactant molecules associate into larger aggregates, it is reflected in the form of a break on the adsorption curve. The break on the curve (Fig. 4) appeared at the surfactant concentration of 0.07 g l^{-1}. This value can be considered as a cmc for the surfactant used. The size of micelles was determined to be 80 nm. An alternative explanation of the increasing absorption is offered by the porosity of cellulose fibres, which may contribute to the adsorption of surfactants to their surface. Kraft fibres are highly porous. The results of the solute-exclusion test suggest that kraft pulps have many slit-like pores with characteristic dimensions of around 5-10 nm[33] or perhaps larger.[16] Alince[17] questioned this conclusion, based on a study of highly cationic polymer adsorption onto cellulose. He assumed that kraft fibres have a relatively narrow distribution of pore widths, of approximately 100 nm. A possible explanation of the increased amount of adsorbed cationic surfactant is the penetration of surfactant into the pore structure of fibres.

A previous work[16] has shown that the penetration into kraft fibres occurs as a function of the size of the molecules. We measured the size distribution of the used cationic surfactant by Malvern Zetasizer Nano and found that the diameter of surfactant aggregates in an aqueous medium is around 80 nm. This relatively large size of the micelles enables only limited surfactant diffusion in this state to the pore structure of the fibres. The diffusion process of the surfactant into the fibre pores is probably slower and will depend on the concentration gradient of surfactant in the solution around the fibre and in the fluid in the pores.

CONCLUSION

The work contributes to the understanding of surfactant adsorption on the surface of cellulose fibres. Cationic surfactant adsorption onto negatively charged pulp fibre surface leads to changes in the specific charge density of the pulp fibres. The 1.5 mg g^{-1} b.d. fibre addition of surfactant leads to the isoelectric point. The state in which the surfactant is adsorbed onto the pulp surface depends on cmc. Up to this concentration, it is supposed that individual molecules are adsorbed onto the surface and, above the cmc, the surfactant is adsorbed in the form of micelles. The critical micelle concentration was estimated as 0.07 g l^{-1} by UV-VIS spectrophotometry.

In the conditions of this experiment, it represents 21.875 mg g^{-1} b.d. fibres. The pulp adsorption capacity for surfactant was determined to be of 35-60 mg g^{-1} of b.d. fibres. It is supposed that this amount is able to cover the outer surface of pulp fibres. Above the critical micelle concentration, we assumed the deposition of micelles with the diameter of 80 nm.

The paper discusses the adsorption process of surfactant onto fibres. The kinetics of deposition takes place according to theoretical assumptions and can be described by the nonlinear equation of the first order. The kinetics of surfactant deposition with different concentrations of surfactant was measured. The first example dealt with a concentration of surfactant below cmc.

At the 0.03 g l^{-1} concentration of surfactant, 9.38 mg g^{-1} b.d. fibers was added. Under these conditions, the whole surfactant was deposited on the pulp surface. In the second case, a surfactant concentration of 0.07 g l^{-1} was used, which is equal to cmc. The amount of added surfactant was 21.88 mg g^{-1} b.d. fibres. Under these conditions, most of the added surfactant was deposited on the pulp surface. In the third case, conditions exceeding cmc were observed. The surfactant concentration was 0.14 g l^{-1} and an amount of 43.75 mg g^{-1} b.d. fibres of surfactant was added. Only 88% of the added surfactant was deposited on the surface. The results confirm a multi-layer deposition of surfactant micelles on the pulp fibre surface. The measured size of the micelles and the estimated diameter of the fibre pores (10-100 nm) allowed only limited deposition onto the pores of the fibres, this process being less probable.

ACKNOWLEDGEMENTS: This work is a part of the research activities financed by the Scientific Grant Agency of the Slovak Republic – Project VEGA 1/0770/08 and 1/0775/13. This study is the result of the implementation of the following projects: APVV 0850-11 supported by the Slovak Research and Development Agency (SRDA), Slovakia and Finalization of Infrastructure of the National Center for Research and Application of Renewable Energy Sources (ITMS: 26240120028).

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