The effect of adsorbed carboxymethyl cellulose on the cotton fibre adsorption capacity for surfactant

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Abstract

The research reported in this paper demonstrates that the capacity of cotton fibres to adsorb cationic surfactants as well as the rate of the adsorption process can be increased by adsorbing carboxymethyl cellulose (CMC) onto the fibre surfaces; in addition, the adsorption can be restricted to the fibre surface. CMC was deposited by means of adsorption from an aqueous solution. The adsorption of N-cetylpyrid-inium chloride (CPC) from an aqueous solution onto the CMC-modified fibres was measured using UV-spectrometric determination of the surfactant concentration in the solution. Adsorption onto the cotton fibres was studied in a weakly basic environment (pH 8.5) where cotton fibres are negatively charged and the CPC ion is positively charged. Modification of the fibres by adsorption of CMC introduces new carboxyl groups onto the fibre surfaces, thereby increasing the adsorption capacity of the fibres for CPC. The initial rate of adsorption of CPC increased proportionally with the amount of charge; however, this rate slowed down at high degrees of coverage on fibres with a high charge. The adsorption of cationic surfactant to the anionic surface groups was stoichiometric, with no indication of multilayer or admicelle formation. It was evident that the acidic group content of the fibres was the primary factor determining cationic surfactant adsorption to these fibres.

Abbreviations: CMC – Carboxymethyl cellulose; CPC – Cetylpyridinium chloride; c.m.c. – Critical micelle concentration

Symbols

- *a* Fibre radius
- A_0 Absorbance at the start of the experiment
- $A_{\rm eq}$ Absorbance at equilibrium time
- A_t Absorbance of bath at time t
- *c* Concentration of absorbing species
- c_{eq} Concentration of surfactant at equilibrium time
- $c_{\rm F}$ Equilibrium uptake of surfactant
- c_t Concentration of surfactant in the fibre at time t
- D Diffusion coefficient

 d_{e} - Degree of exhaustion - Diffusion coefficient determined from the half-adsorption time D_{ha} - Diffusion coefficient calculated according to the square root law equation $D_{\rm sr}$ - Absorbance coefficient k - Slope of the curve $c_t/c_{eq} = f(\sqrt{t})$ K - thickness of sample 1 - Molar mass of surfactant M \overline{M}_{w} – average molecular weight $m_{\rm fibre}$ – Mass of fibres $m_{\rm sur}$ – Mass of surfactant - Half-adsorption time t 1/2

V – Solution volume

Introduction

The presence of acidic groups on fibre surfaces are expected to have an effect on polymer/surface interactions, ion exchange capacity, and technological/biological processes during the manufacturing of cellulose polymer materials. However, the effects of increased charge on the adsorption capacity of the cotton fibre have not yet been investigated systematically in the field of textile chemistry.

In a previous paper (Fras et al. submitted) we described the surface modification of cotton fibres through the irreversible adsorption of carboxymethyl cellulose (CMC) in order to achieve higher surface charge. To accomplish this, we used the same chemical conditions developed by Laine and Lindström (2000, 2001) for wood fibres. We found that the total charge of the cotton fibres could be increased by more than 50% using different CMC products with different average molecular weights.

CMC modifies the fibre surface in two ways: it modifies the surface by strong adsorption, and it increases the charge density of the fibres (Laine and Lindström 2000). The irreversible attachment of CMC onto the surface of cellulose is thought to be due to cooperative hydrogen bonding between the free cellulose segments on the CMC-backbone and the surfaces of the cellulose fibre on the fibre. It has been viewed as a co-crystallization process, but this remains conjectural (Fors 2000).

The functionality of CMC has been well described for cellulosic fibres used for papermaking. CMC adsorption causes an increase in the strength properties of paper sheets made from the fibres (Laine et al. 2002) and, consequently, CMC is used as a dry-strength additive. It has an effect on paper properties similar to that of the general class of hydrophilic wet-end gums and starches. The effect of increased charge - as a consequence of CMC adsorption - on a fibre's ability to swell is also well known (Laine et al. 2002). However, there are no data describing the effect of CMC attachment on the adsorption capacity of fibres.

The hypothesis underlying the investigation reported in this paper is that the adsorption capacity and rate of adsorption of cationic compounds on cotton fibres could be substantially increased by first modifying the fibre surfaces by the adsorption of CMC. Also, the adsorption should be restricted to the fibre surface, which is important in view of the practical utilization of the results in applications where cotton fibres are modified by the adsorption of amphiphilic compound. As a model system, the interactions between a cationic surfactant, cetylpyridinium chloride (CPC) and CMC-modified fibres were studied. This system was chosen because, apart from well-known practical applications, such systems are important in the modelling of complex fluid and fluid/solid mixtures, including biological systems (La Mesa 1999).

To our knowledge, there are no reports on the use of CMC for the modification of textile fibres in order to obtain higher total charge and, consequently, a better adsorption capacity of cationic compounds. CMC-modified cotton fibres could find application in one of the most prospective textile fields – the production of biodegradable, sustainable and highly absorptive materials (Edwards and Vigo 2001; Speakman 1941; Wollina et al. 2003). [¹⁴C]-sodium CMC has been used to measure the adsorption of CMC onto textile fibres and, in the case of cotton, to investigate the

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relationship between adsorption and detergency action. The adsorption of CMC onto cotton has a significant function in preventing redeposition of particulate soil materials (Evans and Evans 1967).

Experimental

Materials

Cotton fibres

The fibres used were natural cellulose cotton fibres (originating from Russia, type Ronda), with a mean fibre length of 29 mm, a micronaire value of 4.4 and a regain of 7.7%. In order to obtain a well-defined reference substance the following cleaning treatments were applied to these fibres:

- alkaline boiling: removal of non-cellulose compounds (hemicellulose, waxes, pectin, proteins) by treatment for 90 min in 0.5 M NaOH at 95°C;
- oxidative bleaching: degradation of natural dyes and pigments by treatment for 30 min with 0.1 M H_2O_2 at pH 11.2 and 95°C.

After each treatment the fibres were washed with distilled water until the conductivity of the water was less than 5 μ S/cm. The processed material was air-dried.

Carboxymethylcellulose

Four commercial CMC samples with different average molecular weights \overline{M}_w were used for modification of the cotton fibres (Table 1). CMCs I–III were manufactured by Mare from Austria and CMC IV by Noviant Oy, Äänekoski, Finland. Their properties are summarized in Table 1.

The average molecular weights of the CMC products were calculated from the viscosity measurements.

Table 1. Average molecular weight (\overline{M}_w) and amount of salt in each CMC product.

СМС		$ar{M}_w$	Amount of	
Product	Notation		san [wt%]	
Niklacell T30	I	167,000	14	
Niklacell T50	II	281,000	10	
Niklacell T100	III	452,000	15	
Nymcel ZSB-16	IV	591,000	9	

The concentration of simple electrolyte in the CMC solutions used for cotton modification was measured using a conductometric measurements (Ander and Sonessa 1965) in order to check if the ionic strength was constant for all samples. The concentration was about 0.001 M in all solutions. The percentage of salt in each CMC product is given in Table 1.

Other chemicals

Cetylpyridinium chloride monohydrate (CPC, $C_{21}H_{38}NCI \cdot H_2O$) ($M_w = 358.0$ g/mol) of analytical grade was manufactured by Aldrich (St. Louis, Mo.) and used without further purification.

In all analyses, ion-exchanged, distilled and degassed water and analytical grade chemicals were used.

Methods

Adsorption of CMC onto the cotton fibres

Prior to the adsorption experiments with CMC, cotton fibres were washed with an excess of 0.1 M HCl for 30 min in order to remove metal ions and to convert ionizable groups on the fibres into their acid form. Following this treatment the fibres were washed with distilled water until the conductivity of the water reached less than 5 μ S/cm. The ionizable groups were changed into their Na-form by washing in 0.001 M NaHCO₃ at pH 9 (adjusted with 0.1 M NaOH) followed by washing with distilled water until a conductivity less than 5 μ S was obtained.

The notation of fibre samples modified with CMC is given in Table 2. CMC was adsorbed onto the fibres using the following procedure in all cases:

The fibres (consistency: 25 g/l) were soaked in a solution of 20 mg CMC/g fibre in 0.05 M CaCl₂ at pH 7–8 and 80°C for 2 h. Following this treatment the fibres (which were now in the Ca-form) were washed with deionized water and ion-exchanged to their H-form or Na-form as described by Fras et al. (submitted). The fibres were stored wet in a refrigerator at 4–6°C and were not dried before analysis. The reference sample (A) was treated in the same manner but without CMC addition.

Conductometric titration

The amount of charge introduced into the modified fibres was determined using a conductometric

Table 2. Topochemical modification of cotton fibres.

Sample	Treatment of fibres ^a
A	Pre-treated (alkaline boiling and oxidative bleaching) fibres
AI	Sample A modified with CMC I
AII	Sample A modified with CMC II
AIII	Sample A modified with CMC III
AIV	Sample A modified with CMC IV

^aCMC attachment conditions: fibre consistency, 25 g/l; CMC addition level; 20 mg/g fibre; 0.05 M CaCl₂; t=2 h; pH = 7–8; $T=80^{\circ}$ C

titration procedure (for a detailed description, see Fras et al. 2004). An amount of wet fibres corresponding to 1 g oven-dry fibres was suspended in 500 cm³ of 1 mM NaCl, acidified with 0.5 cm³ of 0.1 M HCl and titrated at 25 ± 0.5 °C under argon atmosphere with 0.1 M NaOH added from a precision burette in steps of 0.04 cm³ at 1-min intervals. Conductivity was recorded with a Metrohm 712 conductometer (Metrohm, Herisau, Switzerland). A computer controlled NaOH addition and data collection. The amounts of acidic groups were obtained by extrapolation of linear parts of the titration curves to their points of intersection (Katz et al. 1984; Sjöström and Enström 1966). Typically, titrations were finished at a pH of approximately 10.5, which made reliable extrapolation possible. A blank titration without fibres was performed in order to calibrate the system and to eliminate impurity effects. All reported amounts of acid are the mean values of three separate titrations.

UV spectroscopy

The adsorption of CPC onto CMC-modified cotton fibres was evaluated by determining the surfactant concentration in solutions (pH: 8.5 ± 0.5) in contact with the fibres by on-line optical absorbance measurement at the wavelength of maximum absorbance (260 nm) during 3 h of adsorption. The solutions were kept in a thermostat at $25\pm0.5^{\circ}$ C and stirred with a magnetic stirrer. Absorbance was measured every 30 s during the first hour and thereafter every 30 min. A Cary 50 Conc computer-controlled UV spectrometer from Varian was used.

For the adsorption kinetics experiment, 1.5 g of cotton fibre was stirred with solution prepared by mixing of 200 ml of 0.001 N KCl with 50 ml of

0.002 N CPC. The CPC concentration and the substrate mass were chosen so that the following conditions were fulfilled:

- the absorbance was kept between approximately 1.0 and 0.3;
- the difference in the absorbance of the solution in a bath at the beginning and at the end of experiment was at least 0.2;
- the absorbance in a bath at the experiment end should not be less than 0.3;
- the degree of exhaustion of the solution should not be greater than 80%.

The equilibrium surfactant uptake $c_{\rm F}$ (g surfactant/kg fibre) and the degree of exhaustion $d_{\rm e}$ (usually quoted as a percentage) were calculated using the following equations (Fras 2004):

$$c_{\rm F} = \frac{m_{\rm sur}}{m_{\rm fibre}} = \frac{(A_0 - A_{\rm eq}) \times V}{k \times l \times m_{\rm fibre}},\tag{1}$$

$$d_{\rm e} = \frac{A_0 - A_{eq}}{A_0} \times 100, \tag{2}$$

where A_0 = absorbance at the start of the experiment; A_{eq} = absorbance at equilibrium time; V = solution volume; k = absorbance coefficient; l = thickness of sample; m_{sur} = surfactant mass; m_{fibre} = fibre mass.

If $c_{\rm F}$ is divided by the surfactant molar mass M, the surfactant equilibrium uptake is expressed in moles of surfactant per kilogramme of fibres.

Two diffusion coefficients: one for short adsorption times (D_{sr}) and the other for long adsorption times (D_{ha}) were calculated using the following equations (Fras 2004):

$$c_t/c_{\rm eq} = 4\sqrt{\frac{D_{\rm sr}t}{\pi a^2}}.$$
 (3)

If c_t/c_{eq} is plotted against \sqrt{t} , a straight line should be obtained for short adsorption times, and an apparent diffusion coefficient D_{sr} can be calculated from the slope of the line, *K*:

$$D_{\rm sr} = \frac{K^2 \times \pi \times a^2}{16},\tag{4}$$

where *a* is the fibre radius. Diffusion coefficient determination can be simplified using the diffusion coefficient at half adsorption time, $t_{\frac{1}{2}}$. After some

simplifications the value of D_{ha} is finally determined by (Crank 1956):

$$D_{\rm ha} = 0.04919 \frac{a^2}{t_{1/2}} \tag{5}$$

The surfactant concentration in all experiments was well below the critical micelle concentration (c.m.c.). Thus, the surfactant bath could be treated as a monomer solution (Jungerman 1970).

Results and discussion

Determination of charged groups by conductometric titration

The amount of acidic groups (total charge) on CMC-modified fibres obtained by conductometic titration is presented in Table 3. The amount of groups in the acidified form (H-form) of the fibres was about 100% higher in sample AIV than in fibres without CMC (sample A) and more than 100% higher for samples AI, AII and AIII.

In their earlier study of wood fibres Laine et al. (2002) showed that the conversion of the fibres to their Na-form and subsequent storage in deionized water would lead to the desorption of CMC from the fibre material. Therefore, in order to evaluate the degree of desorption of CMC from cotton fibres during storage, we transformed the fibres into their Na-form as described by Laine et al. (2002). The residual charge density was then determined by conductometric titration. We found that a small amount of CMC was clearly desorbed as a result of a weakening of the interactions

Table 3. Anionic groups (total charge) of fibres in acid and neutral forms as determined by conductometric titration.

Sample	Total charge ^a (carboxyls) (mmol/kg)		Desorption (%)	Charge increase (%)
	H-form fibres	Na-form fibres		
A	11.3	-	-	_
AI	22.8	18.2	20	61
AII	25.5	21.3	17	88
AIII	23.1	17.9	23	58
AIV	20.4	16.1	21	43

^aThe uncertainty (coefficient of variation) of the charge determination was less than 2% for all samples.



Figure 1. Kinetics of adsorption of CPC onto cotton samples.

between CMC and the fibres. Table 3 shows that approximately 17-23% of the CMC were desorbed from the fibre material; i.e., the total charge of the fibres in the Na-form increased from 43 to 88% (Table 3) due to CMC adsorption.

Binding mechanism of cationic surfactant adsorption on CMC-modified fibres

The adsorption of CPC as a function of time from a $4 \cdot 10^{-4}$ M solution onto cotton samples at pH 8.5 is shown in Figure 1.

Equilibrium concentrations of CPC (c_F) and the fraction of the total surfactant in the system that was adsorbed at equilibrium (expressed as the degree of exhaustion of the solution, d_e) for cotton modified with different CMCs are summarized in Table 4.

A significant amount of CPC is adsorbed almost instantaneously and a plateau value is reached within 10-30 min for all cotton samples. Adsorption curves of this type, in which initially rapid reactions tend asymptotically towards an equilibrium position, occur commonly and may be described in terms of two parameters, namely the equilibrium value and the rate at which the equilibrium is approached (Mahanta et al. 1987). As shown in the following, the equilibrium values correspond to a stoichiometric formation of ionic bonds between the CPC and the carboxylic groups in the fibres.

Table 4. The equilibrium CPC concentration^a $c_{\rm F}$ and the exhaustion degree of surfactant at equilibrium, $d_{\rm e}$.

Samples	c _F (mmol/kg)	Increase in adsorbed CPC (mmol/kg)	Increase in adsorbed CPC (%)	de (%)
A	9.8	_	_	20
AI	18.4	8.6	89	36
AII	24.3	14.5	148	45
AIII	17.9	8.1	83	32
AIV	15.9	6.1	62	29

^aThe uncertainty (coefficient of variation) of the equilibrium CPC concentration $c_{\rm F}$ was less than 5% for all samples.

The opposite charge of the fibre and the surfactant suggests that the primary driving force for the uptake of CPC by cotton fibres is electrostatic attraction between the anionic carboxylic groups of cotton, ionized at pH 8.5, and the cationic pyridinium groups in the CPC. The shapes of the curves in Figure 1 suggest adsorption in a monolayer - i.e., sites of the fibres are occupied by CPC; when these are filled, the adsorption ceases.

It can be seen from Table 4 that the adsorbed amount of CPC (and, concomitantly, d_E) increases due to fibre modification by the CMCs. The equilibrium CPC concentration is almost the same for samples AI and AIII (18.4 and 17.9 mmol/kg, respectively), and an average increase of more than 80% of adsorbed CPC is reached in both cases. Sample AIV adsorbs up to 15.9 mmol/kg of CPC (+62%) during the first 30 min. Sample AII shows the highest adsorption, giving equilibrium CPC concentration of 24.3 mmol/kg (+148%).

Figure 2 shows the relationship between the fibre charge, as determined by conductometric titration, and the maximum amount of adsorbed CPC on the five fibre samples. The relationship is linear with a correlation coefficient of 0.99 and closely follows the line defining 1:1 stoichiometry. All dissociating carboxyl groups in the fibres are clearly easily accessible to CPC molecules. Thus, the primary driving force of adsorption evidently is ion exchange, resulting in the formation of a 1:1 ionic complex between the anionic carboxyl groups in the fibres and the CMC and the cationic pyridinium groups of CPC. There are no indications of multilayer formation. Neither does the adsorption kinetics give any indication of cooperative interactions between adsorbed CPC leading to the formation of admicelles on the surfaces of



Figure 2. The adsorbed amount of CPC at the plateau level as a function of the total charge of the fibres, as determined by conductometric titration.

the fibres. This was a somewhat unexpected result, as this type of interaction is often observed in the adsorption of cationic surfactants on anionic surfaces (Atkin et al. 2003). The reason that it occurred may be due to the fact that the surface charge density of the fibres is rather low.

On the other hand, adsorption driven predominantly by electrostatic forces, as observed for these fibres, has been reported for the adsorption of other surfactants on various substrates (Espinoza-Jimenez et al. 1997; Jungerman 1970; Kabanov and Zezin 1984). Maximum adsorption of CPC depends largely on the cationic ion exchange properties of the fibres, which follows the alkali number (acidic group amount-anionic charge) (Evans and Evans 1967). The fact that there is a 100% stoichiometric reaction between CPC and the carboxyls on CMC-modified fibres implies that no steric hindrances prevent the formation of ionic bonds.

The uncertainty (coefficients of variation) of the charge determination using conductometric titration was less than 2% for all samples and less than 5% in the case of the adsorbed amount of CPC determination.

In Figure 3 the results given in Figure 2 are replotted as the maximum quantity (mass) of CPC as a function of the mass of CMC adsorbed onto the cotton fibres. The linear relationship indicates that the initial CPC concentration in the solution $(4\cdot10^{-4} \text{ M})$ was sufficient to saturate the sites on the fibres with surfactant in all cases.

Adsorption kinetics and diffusion coefficients of CPC

For a detailed theoretical discussion on the kinetics of cationic surfactant adsorption onto fibres, especially for the diffusion coefficient calculation, see Espinoza-Jimenez et al. (1997), Fras (2004), Fras et al. (2005), Jungerman (1970), Parfitt and Rochester (1983) and Tusek (2003).

The adsorption rate was characterized by calculating the diffusion coefficients. The use of the square root law (Eq. 3) provides a very satisfactory fit in many cases in the initial stages of surfactant adsorption, while the use of the equation based on the half-adsorption time (Eq. 5) is more suitable for moderate to long times. Both "apparent diffusion coefficients' offer a simple and convenient method for comparing surfactants and/ or adsorbing materials (Espinoza-Jimenez et al. 1997; Jungerman 1970; Tusek 2003). Figure 4 shows an example of the plot c_t/c_{eq} versus \sqrt{t} (Eq. 3) obtained from the time/adsorption isotherms of CPC on the CMC-modified sample AII.

Only the experimental points at short adsorption times were taken into account for determination of the slope. In this case the slope was 0.958, and the experimental points fell clearly on a straight line. All experimental results were evaluated in the same way.

The diffusion coefficients for CPC adsorption onto the cotton fibres modified with different CMCs – both calculated according to the square root law equation $(D_{\rm sr}, {\rm Eq. 4})$ and determined

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Figure 3. The mass of adsorbed CPC as a function of the adsorbed mass of CMC.



Figure 4. Plot of c_t/c_{eq} versus \sqrt{t} obtained from the time/ adsorption isotherms of CPC on the CMC-modified sample AII.

from the half-adsorption time $(D_{ha}, Eq. 5)$ – are given in Figure 5.

The initial adsorption of CPC is slowest on the unmodified fibres of sample A ($D_{\rm sr} = 4.4 \cdot 10^{-10} \text{ cm}^2/\text{s}$). The initial adsorption rates are increased by the fibre CMC-modification, and they are almost equal for AI $(D_{\rm sr} = 6.2 \cdot 10^{-10} \text{ cm}^2/\text{s})$ and AIII $(D_{\rm sr} = 5.8 \cdot 10^{-10} \text{ cm}^2/\text{s})$. Modification with CMC IV (sample AIV) gives a $D_{\rm sr} = 5.5 \cdot 10^{-10} \text{ cm}^2/\text{s}$ (lowest of the CMC-modified fibres), while for AII, $D_{sr} =$ $7.8 \cdot 10^{-10} \text{ cm}^2/\text{s}$ (the highest value observed). The trends in the diffusion coefficients D_{ha} are opposite to those of $D_{\rm sr}$ (Figure 5). The following tentative interpretation of these results can be given:



Figure 5. The diffusion coefficients for CPC adsorption onto the CMC-modified fibres. Sample A is the reference sample (non-modified sample).

- (1) At the initial stage of adsorption the electrostatic attraction between negatively charged fibre groups and the positive pyridinium ions will be strong, and ionic bonds between the pyridinium group and carboxyls on the fibres are formed. Assuming that electrostatic attraction is the predominant diffusion driving force in the initial stage of adsorption, $D_{\rm sr}$ should increase with the increasing charge on the fibres, as is, indeed, observed.
- (2) Following the initial adsorption stage (5-10 min) most of the anionic sites are already occupied by CPC, and the strength of the attraction of CPC to the fibres decreases because most of the charge is neutralized.
- (3) With increasing adsorption, the accessibility of remaining free anionic charge on the fibre surface and in the fibre wall may also be reduced due to steric hindrance because adsorbed CPC molecules take up some space on the surface of the fibres. Both this hindrance and the lower electrostatic attraction would result in a decreasing rate of adsorption as maximum adsorption is approached.
- (4) The fibres with high surface charge will initially (say, during the first 5 min) adsorb CPC more rapidly than those with lower charge, resulting in a higher surface coverage in a shorter time. Accordingly, as observed experimentally, the adsorption rate at longer times will be lower for the CMC-modified fibres with high charge.
- (5) The high adsorption rate at long times for sample A could be due to a more open structure of the surface of the untreated fibres than of those covered by CMC.

A comparison of the adsorption kinetics for CPC onto both the non-modified and modified cotton fibres suggests that CMC mainly promotes adsorption on exposed cellulose surfaces. The modified fibre charge is located on the surface because, as discussed in our previous paper (Fras et al. submitted), CMC adsorbs mainly onto the surface of the fibres. Surface adsorption can be expected to occur rapidly, whereas bulk adsorption is a slow process involving slow diffusion into the fibres (Jungerman 1970).

Conclusions

The following conclusions can be drawn from this work:

- (1) The adsorption of CPC onto fibres increases as the anionic charge on the fibres increases (due to CMC adsorption). Due to the attraction between surfactant cations and dissociated fibre carboxyl groups, a higher charge density on the fibres leads to a higher and faster adsorption of CPC.
- (2) The adsorption rate (diffusion of CPC to the fibres) during the initial stage of adsorption increases proportionally to the amount of charge. At longer times of adsorption the rate is slower for the fibres with a high initial charge, probably due to a more rapid initial filling of the sites on these fibres.
- (3) Adsorption of CPC to the charged groups on the fibres is stoichiometric. There is no evidence of cooperative interaction leading to the formation of admicelles on multilayers. Thus, the acidic group content of fibres is of predominating importance for the adsorption capacity at the initial rate of adsorption of CPC on the fibres; at high degrees of coverage steric factors may have some effect on the rate of cationic surfactant adsorption onto fibres.
- (4) Adsorption of CPC to unmodified fibres at high coverages occurs more rapidly than to modified ones, probably because the adsorption of CMC leads to a less open surface structure. Thus, we find that our hypothesis that the surfaces of cotton fibres can be modified by the adsorption of CMC from a solution in such a way that the adsorption kinetics of the cationic surfactants becomes more rapid and the adsorption capacity at the surface is increased is confirmed by our results. This procedure could be utilized for the systematic modification of cotton fibres in practical applications where the adsorption of hydrophobic or amphiphilic molecules is often desirable. In this context, the restriction of adsorption to the fibre surfaces is of particular interest.

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