Whitening Regenerated Cellulose Fibers Using Fluorescent Agent, Surfactants, and Salt—Color Indices Measurements

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ABSTRACT: The whitening efficiency of regenerated cellulose fibers using sodium 4,4′-distyrylbiphenyl sulfonate in the presence of an anionic surfactant (sodium dodecylsulfate) and a cationic surfactant (dodecyl trimethyl ammonium chloride) and salt (NaCl) was determined by fluorescence spectroscopy and color index values (brightness, whiteness, and yellowness). Epifluorescence images gave an intense blue color with an apparent uniform emission distribution. In absence of salt, the whitening efficiency was higher for aqueous solutions containing cationic surfactant below critical micellar concentration (*cmc*). In presence of salt, whitening efficiency was higher for anionic surfactant and more important. The concentration of surfactant required for greater brightness, whiteness, and yellowness was lower than that required in absence of salt. These data were discussed by the decrease of the cmc and by the screening of the modified cellulose fibers by counter ions coming from the salt. The role of surfactants was explained by the admicelization during the sorption process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4371–4380, 2012

Key words: modified cellulose fibers; whitening fluorescent agent; epifluorescence microscopy; color index data; sodium 4,4′-distyrylbiphenyl sulfonate; cationic and anionic surfactants

INTRODUCTION

Cellulose is one of the most abundant natural polymers and is used in numerous manufactured products including paper, textiles, and pharmaceuticals.[1,2] Several of these applications involve sorption of chemical species (dyes, antibiotics, quantum dots, hydrophilic agents, hydrophobic agents, stabilizers, fillers, etc.) on the fibers surface of the cellulose itself or of modified cellulose. Regenerated cellulose fibers are widely used in the textile industry, and its properties depend on the chemical composition, molar mass, degree of polymerization, degree of crystallinity, orientation of the crystallites, and processing conditions.[2,3–9] The surface charge of cellulose fibers is negative, which has been attributed to the presence of carboxyl and hydroxyl groups.[10] Although, it is negatively charged, cellulose adsorbs several types of small and larger molecules positive or negatively charged but different substantivity.[11–13] For example, we observed that regenerated cellulose fibers have a zeta-potential of −6.30 mV when suspended in water. Even though, they have negative charges, sodium 4,4′-distyrylbiphenyl sulfonate a negative fluorescent whitening agent (FWA) can be sorbed significantly on their surface.[14–16]

Sorption of molecules on cellulose fibers involves several processing steps.[17] These steps include the molecular transport from the external medium towards the fibers surface, followed by sorption on the fibers surface, diffusion to the interior of the fiber, and finally fixation of the molecules.[17] Dye sorption can be described by different types of isotherms that depend on the type of fiber-dye interactions. For example, we observed that sorption of the FWA on regenerated cellulose fibers followed a Langmuir isotherm, which is characteristic of electrostatic interactions.[14,18] Nevertheless, we observed that, under similar conditions, Congo red has a higher substantivity than the FWA for regenerated cellulose fibers because in addition to electrostatic interaction it also undergoes hydrogen bonds and probably hydrophobic interactions with the fibers surface.[18] It is postulated that hydrogen bonds involving Congo Red and cellulose fibers are due to a geometrical requirement where those groups of the dye involve with the hydrogen bonds have the same critical distance of 10.3 Å of two neighbor hydroxyl groups of the cellulose units.[19]

Cellulose fibers have a complex morphology that includes crystalline, amorphous, and interface regions whose proportion depends on the processing

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conditions.[17] Therefore, the diffusion process of dyes to the interior of the fibers is also very complex,[17] but it is well known that as for other semicrystalline polymers, dyes do not penetrate in the crystalline phase but can be located in both amorphous phase or crystalline-amorphous interface.[20,21] This information was corroborated by X-ray diffraction patterns that do not show changes of the diffraction patterns after dye sorption in semicrystalline polymers.[20–22] Additional presence of dyes at the interface crystalline-amorphous was obtained by electron transmission microscopy of viscose fibers saturated with FWA aggregated at the micro-fibriles interface and the surface in contact with the aqueous bath has higher concentration of FWA than the fiber bulk.[23] Experiment using confocal laser microscopy gets similar results and showed that uniform dye distribution can be obtained only for long sorption process.[13,24] Although, in this work no further information about dye aggregation was described.

Here we evaluated sorption efficiency of a negatively charged FWA molecule on regenerated cellulose fibers in presence of surfactants (anionic and cationic) as a function of their concentration comparing the color index parameters (whiteness, brightness, and yellowness) based on the CIE system,[25–29] and the fluorescence intensity emission, a property that can be correlated quantitatively with the amount of the sorbed FWA.[14] We also analyzed the FWA fluorescence spectra in aqueous solutions and on fibers to get some insights of how the FWA molecules were organized on the surface in the presence and in the absence of surfactants. In addition, we also discuss the role of salt on the efficiency of the sorption process using the results of the color index data. Atomic force microscopy (AFM) of the fiber surface showed domains compatible to the admicellization of the surfactant and the FWA.

EXPERIMENTAL

Materials

Viscose fibers (from Vicunha Textile, SA, Brazil), sodium 4,4′-distyrylbiphenyl sulfonate (Sigma-Aldrich) (FWA), sodium dodecylsulfate (SDS; Sigma, 98%), and dodecyltrimethylammonium chloride (DTAC) (Fluka, 97%) were used as received. Milli-Q purified water was used throughout the work. Fiber dimensions have average external diameter of 13 ± 1 μm, 3.5 ± 0.1 cm of average length, with a smooth surface and a stripe in the longitudinal direction.[23]

A total of 10 mL of FWA aqueous solution (6.0×10^{-6} mol L^{-1}) were added to a flask containing ~ 0.30 g of fibers. The flask was wrapped in aluminum foil and kept in the dark for 20 min. This time was defined previously as adequate for quantitative determination of the amount of FWA sorbed on the fibers under our experimental conditions.[14] Longer time sorption produces aggregation of the FWA on the fiber surface and modifies the emission signal. After this period, the fibers were dried in an oven under dynamic vacuum at $T = 35°C$ for ~ 24 h, and then stored in a desiccator.

The amount of sorbed FWA was determined by fluorescence spectroscopy taking the emission spectra of the solution before and after the sorption and by calculating the difference of the emission intensity and thus the sorption amount. Details are described in Ref. 14. This protocol was repeated for aqueous solutions with and without surfactants and salt (NaCl 10 mmol L^{-1}). Surfactant concentrations covered a range below and above the correspondent *cmc*. Using the FWA sorbed, we determined the ratio between the mass of the sorbed amount divided by the mass of fiber m_f.

Methods

Steady–state fluorescence spectra of FWA were recorded for both aqueous solutions (with and without surfactants) and sorbed on viscose fibers (in presence and absence of surfactants) using an ISS PCI Photon spectrofluorimeter. Emission was recorded from λ_{em} = 370 to 600 nm with λ_{exc} = 348 nm.

Epifluorescence microscopy was done using a Leica microscope (DMIRB series) coupled with a mercury source excitation lamp (Osram HBO 103W/2) was used for epifluorescence microscopy. The excitation filter was 340–380 nm, and the image was recorded with a Samsung digital color camera SDC-311 connected via *Linksys v2.38* software (Linkam Scientific Instruments).

Scanning electron microscopy (SEM) experiments using a Jeol JSM-6360LV SEM were obtained for a cryogenically fractured surface of regenerated cellulose fibers with carbon- and gold-coated surface by sputtering in a Bal-Tec MED 020 instrument. Accelerating voltage was 20 kV.

AFM experiments were performed with a Nanoscope®IIIa Multimode™ from Digital Instruments. Details are given in Ref. 23.

Color changes on the fibers were measured by diffuse reflectance spectrophotometry (DRS), performed with a GretagMacbeth Color-eye® 2180UV. Spectra provided values of coordinates L^* (color lightness), a^* (red if positive or green if negative), and b^* (yellow if positive or blue if negative) from the CIELAB system of equations.[24,25] These experimental parameters were used to calculate the color-difference parameters: DL^* (darker if negative), Da^* (red-green difference), Db^* (yellow-blue difference), and DE^* (total color difference: $[(DL^*)^2 + (Da^*)^2 + (Db^*)^2]^{1/2}$).

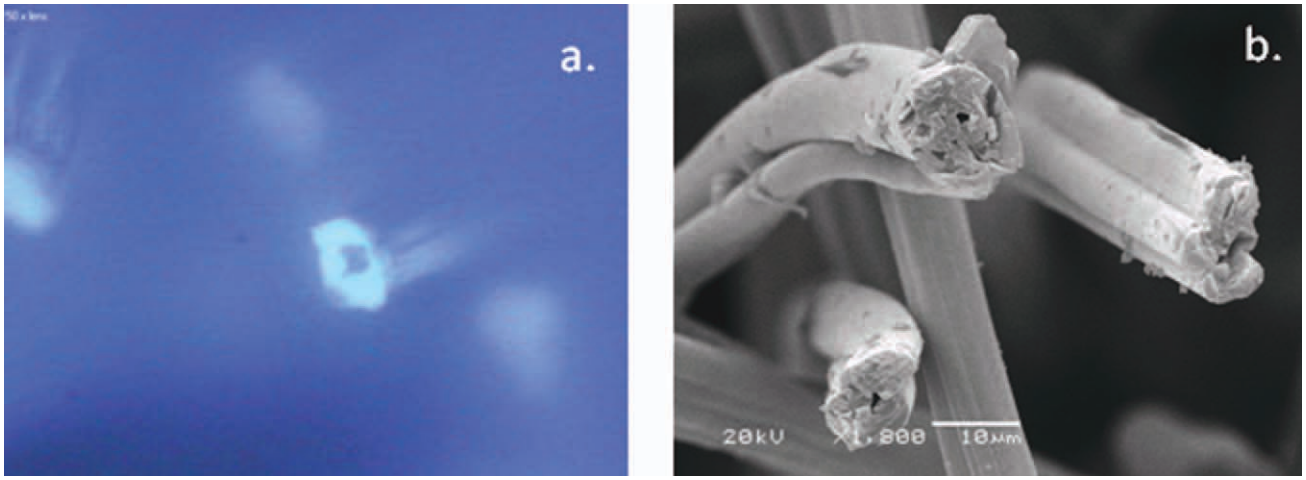

Figure 1 (a) Epifluorescence micrograph of fibers with an intense blue emission from the sorbed FWA. The dark hole indicates the absence of FWA; (b) SEM micrograph of the cryogenically fractured surface cellulose fiber, showing the "empty" central cavity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

The brightness index (TAPPI Brightness T525)[25,24] is an attribute of visual perception in which the material reflects a given amount of light. The whiteness index (Whiteness CIE Ganz 82)[24,25] correlates with the visual ratings of whiteness for a certain white surface, and the yellowness index (Yellowness ASTM E313-73)[24,25] describes the sample color change from white towards yellow. All indices were determined according to the standards indicated. Acceptable values were within the color difference $DE^* = 0.1$ for 10 successive measurements for each sample. The internal reference was the average of a set of 5 or 10 measurements from a sample of fibers without dyeing. All measurements were performed for samples conditioned at 50 ± 5% RH and 25 ± 2°C for 24 h.

RESULTS AND DISCUSSION

Photophysical properties of the FWA

Initial evidence for the sorption of the FWA onto the fibers was obtained by epifluorescence microscopy (Fig. 1). The images of whitened fibers can be described as: dark under UV excitation (not shown) for samples without FWA and bright blue when the FWA is present [Fig. 1(a)]. The recorded images show an apparent uniform brightness distribution but the central hole of the fiber remains dark. The SEM images of fractured fibers showed that these have empty holes [Fig. 1(b)].

Further evidence for the sorption process are obtained by fluorescence spectroscopy. Samples suspended in water solutions (Fig. 2) for 20 min, in the absence and in the presence of surfactants, showed emission spectra with the 0–0 vibrational band at $\lambda_{em} = 414$ nm with a relatively well resolved vibrational structure with the 0–1 band at 436 nm. For comparison, we also obtained the fluorescence spectra for aqueous solutions, in the same FWA concentration (Fig. 3), where broader spectra were obtained for water and water + SDS ($\lambda_{em} = 430$ nm) and a spectrum with vibrational structure was obtained for water + DTAC ($\lambda_{em\ (0\text{-}0)} = 408$ nm and $\lambda_{em(0\text{–}1)} = 428$ nm). Only changes of the intensity occurred with the surfactant concentration.[14] Salt (NaCl 10 mmol L^{-1}) does not affect either the emission intensity or the band profile (spectra were not showed).

We also recorded the emission spectra for the FWA in solid state (Fig. 4), which rendered a broad band, centered at $\lambda_{em} = 487$ nm without vibrational structure. For samples suspended in water (concentration $= 6.0 \times 10^{-6}$ mol L^{-1}) for 20 min, the

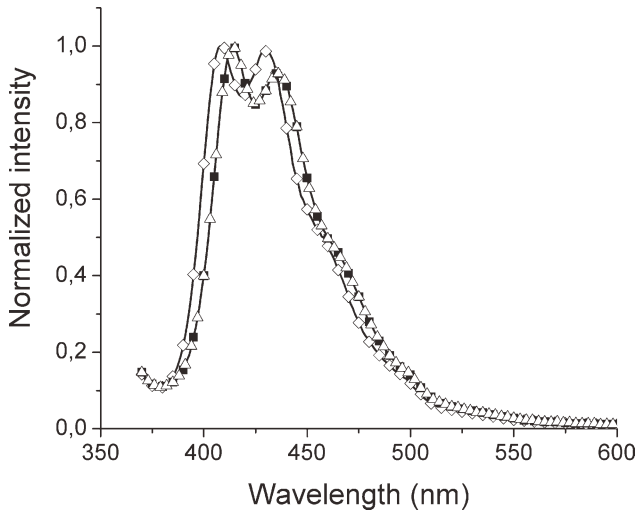

Figure 2 Fluorescence spectra of sodium 4,4′-distyrylbiphenyl sulfonate in sorbed on regenerated cellulose fibers after being suspended in water solution (■), water solution with SDS (△) and water solution with DTAC (◇) for 20 min. $\lambda_{exc} = 348$ nm.

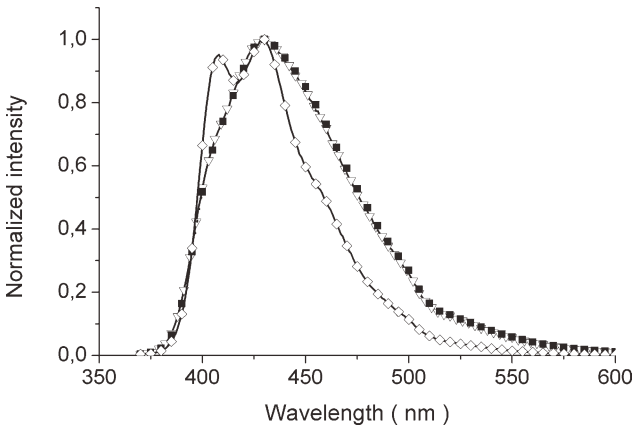

Figure 3 Normalized fluorescence intensity of sodium 4,4′-distyrylbiphenyl sulfonate in aqueous solution (■), aqueous solution + SDS (△), aqueous solution + DTAC (◇). [FWA] = 6.0×10^{-6} mol L^{-1}, [SDS] = 6 mmol L^{-1}, and [DTAC] = 20 mmol L^{-1}. λ_{exc} = 348 nm.

emission spectrum was blue-shifted when compared with emission of solid, presenting the 0–0 band at λ_{em} = 414 nm, and a relatively well resolved vibrational structure with a peak at 436 nm. For comparison, we also recorded an emission spectra of fibers saturated with FWA (Fig. 4) ([FWA] = 6.0×10^{-6} mol L^{-1}, sorption for 24 h), and under this condition the emission was red-shifted (λ_{em} = 441 nm) compared to isolated molecules without vibrational structure but appears at higher energy compared to the crystals. From these data we concluded that the emission around 410–420 nm was due to isolate molecules, which were observed for both aqueous dilute solutions and on the fiber surface under lower loading and noncrystalline aggregates are sorbed under higher loading conditions.

More interesting, the FWA emission profiles (a negative molecule) in aqueous solution with DTAC (a cationic surfactant) and fiber surface (negatively charged when suspended in water) were similar, indicating that the rigidity of the medium was controlling the vibrational structure of the emission band. This spectral feature shows that the rotational movements around the biphenyl bond are hindered on the fibers surface and completely free on the aqueous solution.[30] According to these results, we can assume that in aqueous solutions of DTAC a strong whitening agent-surfactant interaction is occurring because they have opposite charges and the rotation is also hindered; in aqueous solutions of SDS a weak whitening agent-surfactant interaction is occurring because both have negative charges and the rotation is free as in aqueous solution. Nevertheless, when sorbed on fibers, the spectral feature was independent of the suspending solution.

Whitening efficiency in presence of surfactant

The whitening efficiency was obtained by two independent methodologies. The first used the brightness, whiteness, and yellowness indices. These indices were determined for the FWA sorption on regenerated cellulose fibers as a function of the SDS (anionic) and DTAC (cationic) concentrations (Fig. 5 and Tables I and II, respectively), having fibers without the FWA as the standard.

Compared with the standard (fibers without FWA), fibers in the presence of SDS are brighter [Fig. 5(a-left)], whitener [Fig. 5(b-left)], and less yellow [Fig. 5(c-left and Table I)], and these indices although better than fibers without FWA are practically independent of the SDS concentration. This practical independence may be attributed to the small amount of FWA sorbed in presence of SDS, as discussed later on.

Whitening process in the presence of DTAC (cationic surfactant) showed that: fibers were brighter [Fig. 5(a-right)], more whitener [Fig. 5(b-right)], and less yellow [Fig. 5(c-right and Table II)] than the standard, the efficiency depended on the surfactant concentration, was higher near the DTAC *cmc*, around 15 mmol L^{-1} and then, efficiency decreased for higher surfactant concentrations. These results validate our previous results for the quantitative analysis of the sorption: the amount of the FWA sorbed in the presence of SDS was small, nearly independent of the surfactant concentration and was always lower than in presence of DTAC. In the presence of DTAC, the amount of sorbed FWA was higher for lower DTAC concentration, decreased with the increase of the surfactant concentration and became practically constant when its *cmc* was

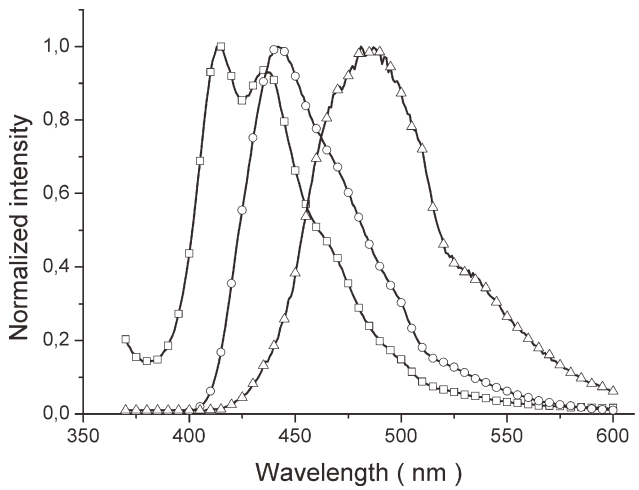

Figure 4 Normalized fluorescence intensity of sodium 4,4′-distyrylbiphenyl sulfonate sorbed in cellulose fibers after 20 min (□), under saturated conditions (○) and in the crystalline form (△). λ_{exc} = 348 nm.

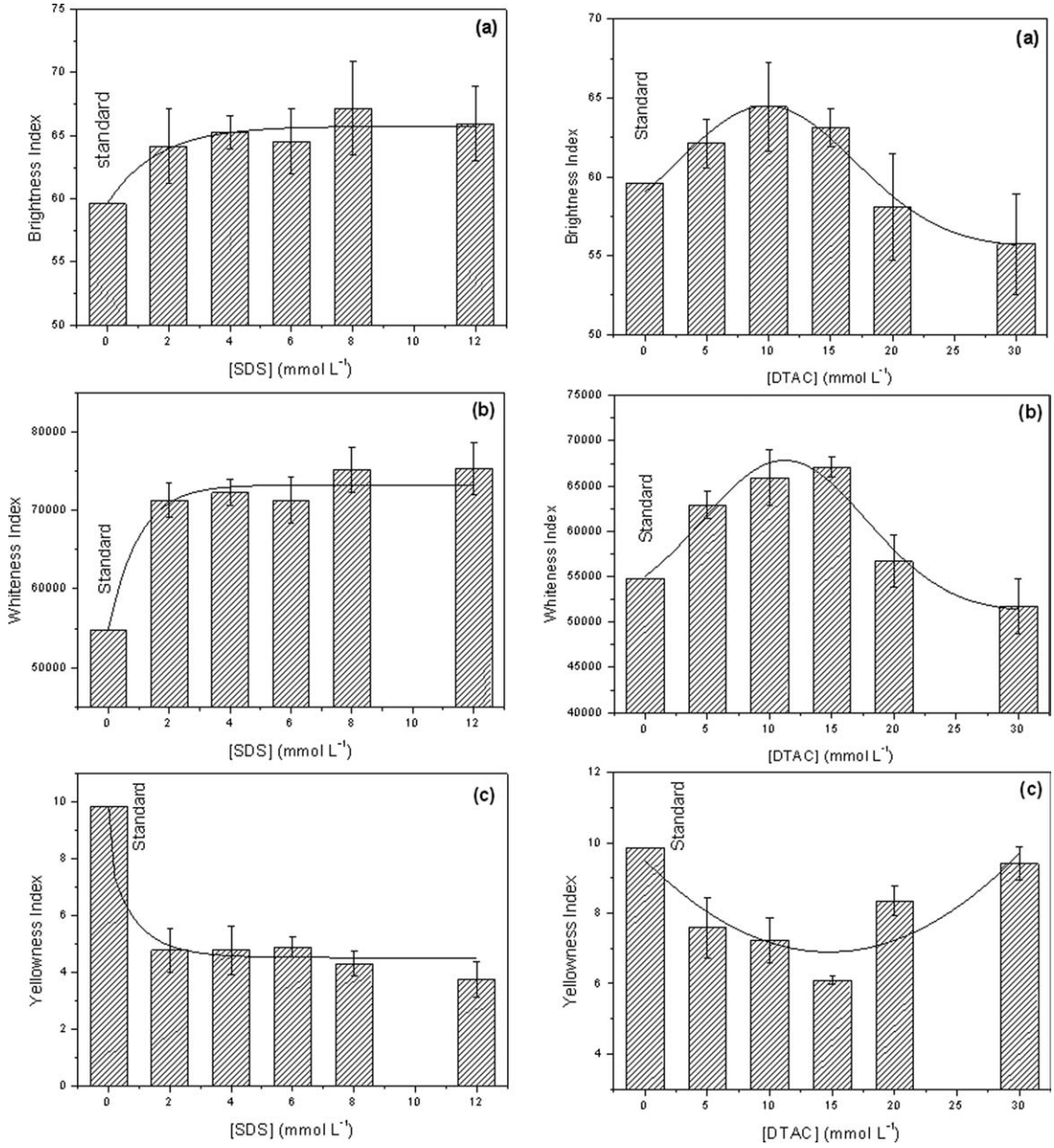

Figure 5 Color indices of the FWA sorbed onto a regenerated cellulose fiber as a function of the SDS (left) and DTAC (right) concentration: (a) Brightness index (TAPPI Brightness T525), (b) Whiteness index (Whiteness CIE Ganz 82), and (c) Yellowness index (Yellowness ASTM E313-73). Individual data is shown in Tables I (SDS) and II (DTAC).

achieved.[14,18] This minimum value was similar to that found in the presence of SDS.[14,18]

The adsolubilization model[31,32] explains these results, in which both surfactant and FWA can be sorbed competitively on fibers surface. Differences of behavior between DTAC and SDS were attributed to differences or fibers/surfactant and FWA/surfactant interactions. Using the adsolubilization model[31–33] we assume that the opposite charges of DTAC and the fibers produced an initial electrostatic interaction between the surfactant head and the fibers surface at low concentrations, and surfactant was sorbed preferentially. This initial sorption neutralized the surface charge and then, both FWA and surfactant could be sorbed. Bilayers of DATC were formed at intermediate surfactant concentrations (relatively to the surfactant *cmc*); and finally surfactant micelles were formed at concentrations higher than the *cmc*. Larger concentrations of FWA could be sorbed in the two initial stages induced by the electrostatic interaction involving opposite charges of the positive head of the surfactant and the negative charge of FWA. When a bilayer of surfactant was formed, the possibility of electrostatic interactions were minimized, this molecule cannot interact by hydrogen bonds or other strong forces and under this condition only small amount could be sorbed. Similar results were observed for SDS/FWA, both

TABLE I
Values of the Color Index Parameters for the FWA Sorption onto Fiber as a Function of the SDS Concentration

Sample	*L**	*a**	*b**	*DL**	*Da**	*Db**	*DE**	Yellowness ASTM E313-73	Whiteness CIE Ganz 82	TAPPI Brightness T525 (1986)
Fiber (Standard)	83.13	−0.05	0.99	–	–	–	–	9.86	54,789	59.6
SDS 2 mmol L^{-1}	83.2 ± 1.7	0.7 ± 0.4	−1.7 ± 0.4	−0.7 ± 1.7	0.90 ± 0.4	−3.1 ± 0.4	3.6 ± 0.8	4.8 ± 0.8	71,235 ± 2166	64.1 ± 3.0
SDS 4 mmol L^{-1}	83.8 ± 0.8	0.68 ± 0.08	−1.7 ± 0.4	−0.08 ± 0.80	0.85 ± 0.08	−3.1 ± 0.4	3.3 ± 0.5	4.9 ± 0.9	72,215 ± 1657	65.3 ± 1.3
SDS 6 mmol L^{-1}	83.4 ± 1.3	0.68 ± 0.03	−1.6 ± 0.2	−0.4 ± 1.3	0.84 ± 0.03	−3.0 ± 0.2	3.4 ± 0.3	4.9 ± 0.4	71,286 ± 2987	64.5 ± 2.6
SDS 8 mmol L^{-1}	84.6 ± 1.9	0.78 ± 0.04	−2.0 ± 0.2	0.7 ± 1.9	0.94 ± 0.04	−3.4 ± 0.2	4.0 ± 0.5	4.3 ± 0.4	75,177 ± 2898	67.2 ± 3.7
SDS 12 mmol L^{-1}	83.8 ± 1.5	0.88 ± 0.04	−2.3 ± 0.3	−0.06 ± 1.5	1.04 ± 0.04	−3.7 ± 0.3	4.1 ± 0.5	3.7 ± 0.6	75,293 ± 3334	66.0 ± 3.0

TABLE II
Values of the Color Index Parameters for the FWA Sorption Process onto Fiber in Function of the DTAC Concentration

Sample	*L**	*a**	*b**	*DL**	*Da**	*Db**	*DE**	Yellowness ASTM E313-73	Whiteness CIE Ganz 82	TAPPI brightness T525 (1986)
Fiber (Standard)	83.1	−0.05	0.99	–	–	–	–	9.86	54,789	59.6
DTAC 5 mmol L^{-1}	83.0 ± 1.0	0.33 ± 0.07	−0.15 ± 0.45	−0.9 ± 1.0	0.49 ± 0.07	−1.5 ± 0.5	2.0 ± 0.6	7.6 ± 0.9	62,866 ± 1511	62.1 ± 1.5
DTAC 10 mmol L^{-1}	84.0 ± 1.5	0.36 ± 0.09	−0.3 ± 0.4	0.2 ± 1.5	0.52 ± 0.09	−1.7 ± 0.4	2.2 ± 0.7	7.2 ± 0.6	65,927 ± 3131	64.4 ± 2.8
DTAC 15 mmol L^{-1}	83.1 ± 0.6	0.43 ± 0.05	−0.94 ± 0.07	−0.8 ± 0.6	0.59 ± 0.05	−2.3 ± 0.1	2.6 ± 0.2	6.1 ± 0.1	67,073 ± 1122	63.1 ± 1.2
DTAC 20 mmol L^{-1}	81.0 ± 1.9	0.04 ± 0.05	0.3 ± 0.2	−2.9 ± 1.9	0.20 ± 0.05	−1.0 ± 0.2	3.1 ± 1.8	8.4 ± 0.4	56,697 ± 2877	58.1 ± 3.4
DTAC 30 mmol L^{-1}	79.9 ± 1.9	−0.13 ± 0.04	1.0 ± 0.2	−3.9 ± 1.9	0.03 ± 0.04	−0.3 ± 0.4	4.0 ± 1.9	9.4 ± 0.5	51,722 ± 3013	55.6 ± 3.2

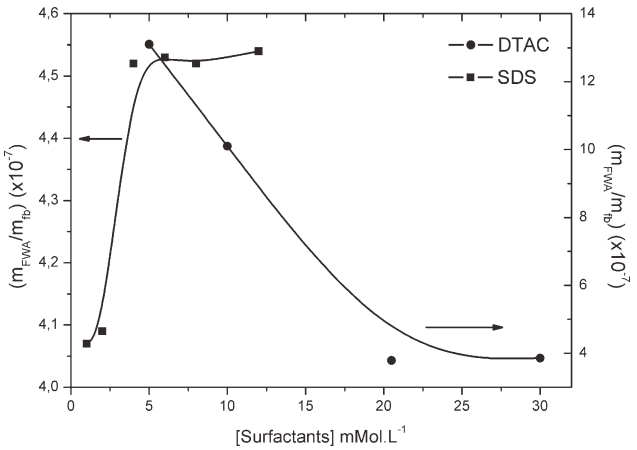

Figure 6 Amount of FWA sorbed onto fibers (mass per mass) versus surfactant concentration (SDS and DTAC). Immersion time 20 min, [FWA] = 6.0×10^{-6} mol L^{-1}.

with negative charges and because of the absence of strong attractive interactions, only small amount of both could be sorbed.

Further evidences of surfactant sorption were obtained by AFM, where we observed globular domains deposited for samples with DTAC (larger domains) and with SDS (smaller globules).[23] All of these observations were consistent with changes of zeta-potential measured for fibers immersed in aqueous solutions of FWA and surfactants. Around *cmc*, the zeta-potentials undergo pronounced changes that must influence all electrostatic interactions among the solution components.[14]

The second method that we used involved a quantitative determination of the FWA sorbed, which was carried out by fluorescence spectroscopy. The amount of the FWA sorbed relatively to the amount of fiber was determined by the difference of the fluorescence intensity in FWA aqueous solutions before and after the sorption process. A calibration curve for the fluorescence intensity versus FWA concentration was previously determined at $\lambda_{em} = 410$ nm. The ratio between the mass of FWA sorbed (m_{FWA}) and the mass of fiber (m_{fb}) was plotted as a function of the surfactant concentration (SDS and/or DTAC) (Fig. 6).

These data showed in the presence of small amount of DTAC (positively charged surfactant), there is a greater amount of sorbed FWA, which decreases to the ratio without surfactants for DTAC greater than the *cmc* (20 mmol L^{-1}). However, the amount of sorption increases with the amount of SDS, achieving a constant value below the *cmc* (4–6 mmol L^{-1}). The saturation value is practically constant and independent of the surfactant charge.

When these curves are compared with the CIE indices showed in Figure 5 we can see that for SDS the saturation occurs at around 3.0 mmol L^{-1} of surfactant corresponding to the maximum sorption mass per mass of fiber, taking into account the standard (solution without surfactant). Furthermore, for DTAC the maximum brightness and whiteness

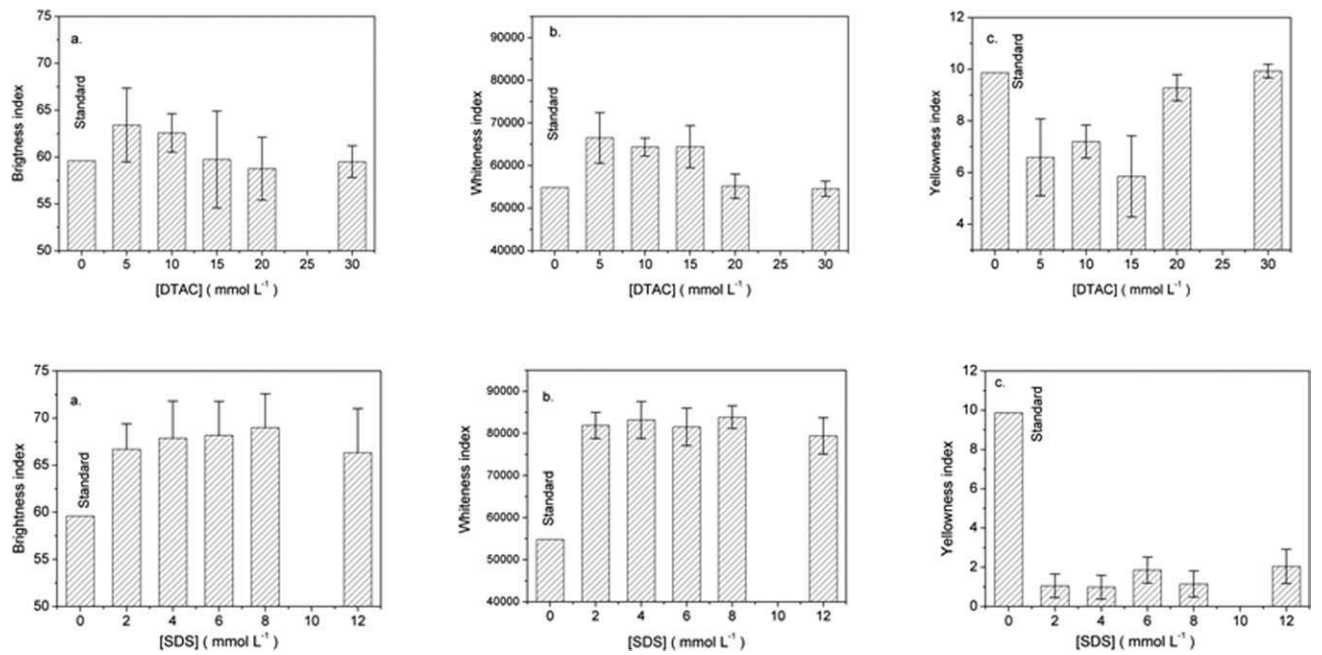

Figure 7 Color indices of FWA sorbed onto a regenerated cellulose fiber as a function of the SDS (left) and DTAC (right) concentration + 10 mmol L^{-1} NaCl: (a) Brightness index (TAPPI Brightness T525), (b) Whiteness index (Whiteness CIE Ganz 82), and (c) Yellowness index (Yellowness ASTM E313-73). Individual data is shown in Tables III (SDS) and IV (DTAC).

and minimum yellowness indices were observed for surfactant concentration corresponding to the *cmc* (≈15 mmol L^{-1}). For higher surfactant concentrations the yellowing is observed, which explains the presence of yellow spots in textiles in presence of high surfactant concentration. This behavior can be explained by the surface zeta-potential of the fiber surface, which has the greater positive value in the DTAC aqueous solutions of 15 mmol L^{-1}.[14]

Whitening efficiency in presence of surfactants and salt

Experiments were repeated for solutions containing NaCl 10 mmol L^{-1}, maintaining constant other conditions. Figure 7 (Tables III and IV) shows that brightness, whiteness, and yellowness indices (Fig. 7-left) were improved for fibers immersed in SDS solutions with salt compared with those of without salt (Fig. 5-left). We also observed that index values were practically independent of the surfactant concentration, which means that salt improved efficiency even for SDS concentration below its *cmc*. On the other hand, salt had small effect over brightness, whiteness, and yellowness indices (Fig. 7-right) compared with those solutions without salt (Fig. 5-right) but the relevant result was that for the same efficiency, smaller amount of surfactant was required: we observed maximum whiteness with 5.0 mmol L^{-1} of surfactant instead of 10–15 mmol L^{-1}.

Salt in these systems played two different roles: one was by screening the surface charge of fibers, which allowed sorption of the negatively charged SDS molecules. This was demonstrated by measuring zeta-potentials. In addition, salt decreased *cmc* values of both surfactants.[14] The screening effect produced changes of the zeta-potentials curve profiles for aqueous solution of surfactants with immersed fibers in presence and absence of salt, while *cmc* in the same conditions changed from 15 to 18 mmol L^{-1} to 10–12 mmol L^{-1} for DTAC and from around 6–7 to 2–4 mmol L^{-1} for SDS, depending which technique was used (turbidity, fluorescence intensity, zeta-potential or amount of sorption).[14] Screening processes should be more relevant for SDS solutions. The negative charges of fibers surface were neutralized by counter ions and thus either FWA or SDS could be more efficiently sorbed. As a result, whitening efficiency was higher than those samples without salt and lower amount of surfactant was required because of the decrease of the *cmc*. On the other hand, screening process was less important for the DTAC sorption and no further improvement of the whitening efficiency was produced.

Again we quantitatively determined the amount of FWA sorbed onto the fiber surface using

TABLE III
Values of the Color Index Parameters for the FWA Sorption Process onto Fiber in Function of the SDS Concentration in Presence of 10 mmol L^{-1} of NaCl

Sample	L^*	a^*	B^*	DL^*	Da^*	Db^*	DE^*	Yellowness ASTM E313-73	Whiteness CIE Ganz 82	TAPPI brightness T525 (1986)
Fiber (Standard)	83.13	−0.05	0.99	–	–	–	–	9.860	54,789	59.6
SDS 2 mmol L^{-1}	83.4 ± 1.3	1.24 ± 0.09	−3.7 ± 0.3	−0.4 ± 1.3	1.40 ± 0.09	−5.1 ± 0.3	5.5 ± 0.4	1.051.0 ± 0.6	81,879 ± 3128	66.7 ± 2.7
SDS 4 mmol L^{-1}	84.0 ± 1.8	1.28 ± 0.07	−3.8 ± 0.3	0.1 ± 1.8	1.44 ± 0.07	−5.2 ± 0.3	5.6 ± 0.6	1.0 ± 0.6	83,175 ± 4381	67.9 ± 3.9
SDS 6 mmol L^{-1}	84.3 ± 1.7	1.1 ± 0.1	−3.3 ± 0.4	0.5 ± 1.7	1.3 ± 0.1	−4.7 ± 0.4	5.2 ± 0.4	1.9 ± 0.7	81,517 ± 4440	68.2 ± 3.6
SDS 8 mmol L^{-1}	84.6 ± 1.9	1.23 ± 0.06	−3.7 ± 0.3	0.7 ± 1.8	1.39 ± 0.06	−5.1 ± 0.3	5.6 ± 0.4	1.1 ± 0.7	83,830 ± 2691	69.0 ± 3.6
SDS 12 mmol L^{-1}	83.5 ± 2.5	1.12 ± 0.07	−3.2 ± 0.4	−0.4 ± 2.5	1.28 ± 0.07	−4.6 ± 0.4	5.3 ± 0.9	2.0 ± 0.9	79,405 ± 4322	66.3 ± 4.7

fluorescence spectroscopy. The ratio between m_{FWA}/m_{fb} was plotted as a function of the surfactant concentration (Fig. 6). The data showed that the sorption saturation is obtained for lower concentration of surfactant (for both), the *cmc* values are also lower. However, the maximum and the minimum amount of sorbed FWA in the presence or in the absence of DTAC are the same. Nevertheless, much lower amount was sorbed in the presence of SDS, with better results in terms of CIE indices. Very small yellowness index is observed for fibers dipped into SDS solutions even though its concentration is smaller as 2 mmol L^{-1}.

TABLE IV
Values of the Color Index Parameters for the FWA Sorption Process onto Fiber in Function of the DTAC Concentration in Presence of 10 mmol L^{-1} of NaCl

Sample	L^*	a^*	B^*	DL^*	Da^*	Db^*	DE^*	Yellowness ASTM E313-73	Whiteness CIE Ganz 82	TAPPI brightness T525 (1986)
Fiber (Standard)	83.1	−0.05	0.99	–	–	–	–	9.86	54,789	59.6
DTAC 5 mmol L^{-1}	83.3 ± 1.9	0.5 ± 0.1	−0.7 ± 0.7	−0.6 ± 1.9	0.7 ± 0.1	−2.1 ± 0.8	2.8 ± 1.0	6.6 ± 1.5	66,459 ± 5916	63.4 ± 3.9
DTAC 10 mmol L^{-1}	83.1 ± 1.1	0.46 ± 0.03	−0.40 ± 0.3	−0.8 ± 1.1	0.62 ± 0.03	−1.8 ± 0.3	2.3 ± 0.5	7.2 ± 0.6	64,330 ± 2105	62.6 ± 2
DTAC 15 mmol L^{-1}	81.1 ± 3.1	0.5 ± 0.2	−1.1 ± 0.8	−2.7 ± 3.1	0.7 ± 0.2	−2.4 ± 0.8	4.1 ± 2.5	5.9 ± 1.6	64,426 ± 4950	59.7 ± 5.1
DTAC 20 mmol L^{-1}	81.6 ± 2.0	−0.10 ± 0.02	0.9 ± 0.3	−2.3 ± 2.0	0.07 ± 0.02	−0.51 ± 0.28	2.4 ± 1.9	9.3 ± 0.5	55,142 ± 2850	58.8 ± 3.4
DTAC 30 mmol L^{-1}	82.2 ± 0.9	−0.06 ± 0.09	1.2 ± 0.1	−1.7 ± 0.9	0.07 ± 0.03	−0.2 ± 0.1	1.8 ± 0.9	9.9 ± 0.3	54,542 ± 1784	59.5 ± 3.0

CONCLUSIONS

This report evaluated the whitening efficiency of the sorption processes of the FWA on regenerated cellulose fibers using color index parameters. These indices showed that both surfactant and salt interfered with the efficiency of whitening process. In absence of salt the cationic surfactant favored the FWA sorption for surfactant concentrations lower than the *cmc*, probably due to the adsolubilization process. In presence of salt, no further efficiency was observed. For the anionic surfactant SDS solutions we observed that in absence of salt, the whitening efficiency was lower and almost independent of the surfactant concentration but in presence of salt the efficiency increased and lower surfactant concentration was required. Epifluorescence images showed in all cases a strong and apparently uniform blue emission was obtained from entire fibers surface. From ecological and economical point of view, however, when the CIE indices of the best surfactant conditions were compared, we can see that SDS expressed similar whiteness and brightness as DTAC, but lower yellowness than DTAC, for lower surfactant concentrations, which suggests that formulations with lower amount of components can display similar results. These achieves are relevant for formulations of whitening medium of textiles fibers. The best surfactant should have opposite charge compared to the FWA and must be in concentration close to its *cmc*.

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