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Article

Spectroscopic Study of the Interaction of Reactive Dyes with Polymeric Cationic Modifiers of Cotton Fabrics

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Abstract: Cotton cationization with low molecular weight or polymeric cationic modifiers allows the effective dyeing of cotton substrates with reactive dyes under salt-free and more environmentally-friendly conditions. The current work focuses on the spectroscopic study of the intermolecular interactions, which dictate the physicochemical process associated with fabric dyeing. Water-soluble cationic copolymers of vinyl benzyl chloride and vinyl benzyl triethylammonium chloride (VBCTEAM) have been used as cellulose cationic modifiers. Dye uptake was assessed using Remazol Brilliant Blue and Novacron Ruby dyes. The study involves ATR-FTIR, UV-Vis, fluorescence and XPS spectroscopy. The results of binary polymer-rich dye-polymer aqueous solutions or dye-polymer precipitates at stoichiometric charge-ratio revealed that the sulfonate/sulfate anions of the dyes interact with the cationic VBCTEAM units of the polymer *via* electrostatic interactions. Moreover, the comparative study of dye application on modified and unmodified fabrics suggests that, unlike the latter where dyes are chemically bound to cellulose, electrostatic forces dominate the interaction of modified fabrics with dye molecules.

Keywords: cotton; reactive dyes; cationization; polymeric modifier; salt-free dyeing; electrostatic interactions; covalent bonding

1. Introduction

Currently, dyeing of cotton fabrics is performed using mostly reactive dyes. These dyes, such as Novacron Ruby NRS-3B and Remazol Brilliant Blue R (**Scheme 1a,b**), contain reactive groups able to form covalent bonds with cellulose under alkaline conditions and they are preferred for cotton dyeing applications due to the improved wash-fastness properties and ease of application [1,2]. However, reactive dyes are usually anionic and a large amount of electrolytes is needed to screen the repulsive forces between the negative charges of both cotton and dye molecules under dyeing conditions; this leads to low dye retention (~50%) and to hydrolysis of a significant amount of the remaining dye. In addition, this process raises environmental concerns, because of the discharge of a highly colored and saline dye bath [2,3].

In the past 20 years, numerous efforts were focused on cationization of cotton before the dyeing process [4-8]. Most of these studies used low molecular weight cationic compounds, such as 3-chloro-2-hydroxypropyl trimethylammonium chloride, CHPTAC [1,9-16]. Cationization of cotton results to the charged inversion of the cotton surface and the dye is now attracted electrostatically. Though cationization of cotton with low molecular weight compounds is a very important process in terms of cost and environmental impact since the use of salt is avoided, it has significant drawbacks, such as uneven dyeing and poor thermal stability [17], in addition to toxicity or unpleasant odour.

Cationic polyelectrolytes have been also proposed as cationic cotton modifiers [18-24]. In most cases, covalent attachment of polymer onto the cellulose surface is assured through cellulose-initiated polymerizations [25-30] and rarely on the reaction of cellulose with cationic copolymers bearing reactive units, like glycidyl methacrylate (GMA) [31].

To further improve cotton dyeing processes, a major challenge is to get a deeper understanding of cationic modifier – dye interactions. To this end, we took advantage of a variety of spectroscopic techniques, such as UV-Vis and fluorescence spectroscopies, ATR-FTIR vibrational spectroscopy and X-Ray Photoelectron spectroscopy (XPS), for the study of binary dye-polymer mixtures both in aqueous solution and in solid state, as well as of cationized cotton substrates dyed with reactive dyes. To elucidate the influence of the charge density of the cationic modifier, the homopolymer poly(4-vinyl benzyl triethylammonium chloride), PVBCTEAM (Scheme 1c, $x=0$), and the copolymer P(VBC-co-VBCTEAM53) containing 53% mol VBCTEAM units (Scheme 1c, $x=53$) were selected. Moreover, in order to explore the importance of the charge density of the dye, the reactive dyes Novacron Ruby NRS-3B and Remazol Brilliant Blue R bearing two and five negatively charged groups, respectively, were chosen for the study.

2.1. Materials

The homopolymer poly(4-vinyl benzyl triethylammonium chloride), PVBCTEAM, and the copolymer P(VBC-co-VBCTEAM53), containing 53% mol VBCTEAM units, were synthesized and characterized as mentioned elsewhere [32]. The reactive dyes: Remazol Brilliant Blue R (C.I 61200/ CAS 2580-78-1) and Novacron Ruby NRS-3B (C.I reactive red mixture-89157-03-9; 718619-88-6) were purchased from Huntsman International LLC. The composition of the second dye mixture is not exactly known, however, our XPS data indicate major contribution of the 718619-88-6 component.

Cotton fabrics were kindly granted from COLORA S.A. Double jersey knitted (Rib 1x1 alignment, knot length 4.4mm) pure cotton fabrics have been used, avoiding the application of alkali bleaching. Ultrapure water was obtained by a Milli-Q RG apparatus water purification unit.

2.2. Sample preparation

2.2.1. Binary systems

Aqueous stock solutions of the polymers and the dyes were initially prepared. Appropriate volumes of polymer and dye solutions were then mixed to achieve the desired dye/polymer charge ratio, D/P⁺. All four dye-polymer combinations were examined. For low D/P⁺ charge ratios (excess of polymer charges), the solutions remained homogeneous for a sufficient period allowing the UV-Vis and fluorescence spectroscopic investigation. Representative photos of the solutions are given in Fig. S1.

For D/P⁺ charge ratios close to the stoichiometry, precipitation occurred immediately and left to proceed for 24 h. The colored solid precipitates were collected using a 0.2 μm porous-filter and were characterized by ATR-FTIR and XPS spectroscopy. The Whatman® Anodisc inorganic filter (diameter 25 mm, pore size 0.2 μm, no autoclavable) used for this purpose, as well as the Whatman® plastic filter holders (Swin-Lok Holder, diameter 25 mm) were purchased from Merck Chemical Company. The binary systems investigated are summarized in Table 1.

Table 1. The binary systems investigated.

Code-Name	Reactive Dye component	Cationic Polymer Modifier component
NR-homo	Novacron Ruby NRS-3B	PVBCTEAM
NR-copo	Novacron Ruby NRS-3B	P(VBC-co-VBCTEAM53)
RBB-homo	Remazol Brilliant Blue R	PVBCTEAM
RBB-copo	Remazol Brilliant Blue R	P(VBC-co-VBCTEAM53)

2.2.2. Ternary systems

Focusing on the surface modification of cotton substrates with cationic polymers and then on the subsequent dyeing of these fabrics, in Section S1 and Section S2 the used protocols are given, which they have been already mentioned elsewhere [32]. Four dyed fabrics were obtained. Two samples were modified with the homopolymer PVBCTEAM and dyed with either Remazol Brilliant Blue R or Novacron Ruby NRS-3B. Similarly, two samples were modified with the copolymer P(VBC-co-VBCTEAM53) and dyed with the two dyes. For comparison, dyeing of unmodified cotton fabrics with the same protocol, in the absence or presence of NaCl, was also performed and studied (Section S2).

2.3. Analytical techniques

2.3.1. Scanning Electron Microscopy (SEM)

High resolution field-emission scanning electron microscopy (FE-SEM) revealed the morphological features of the materials. A Zeiss SUPRA 35VP system operating at 5 kV voltage was used for this purpose.

2.3.2. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The ATR-FTIR spectra of solid samples were recorded on a Alpha-II Diamond ATR Spectrometer of Bruker Optics GmbH (Ettlingen, Germany).

2.3.3. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy measurements were performed in UHV (Pressure ~5×10⁻¹⁰ mbar) system equipped with a hemispherical electron analyzer (SPECS, Phoibos 100-1D-DLD) and a

non-monochromatized dual-anode Mg/Al X-ray gun. Survey and narrow scans of C 1s, O 1s, N 1s, S 2p, Na 1s and Cl 2p spectra were recorded by using the X-ray source MgK α at 1253.6 eV photon energy. Two analyzer pass energies were used, 10 eV and 20 eV, giving a Full Width at Half Maximum (FWHM) of 0.85 eV and 1.0 eV for the Ag3d5/2 line, respectively. Spectra were accumulated and fitted using commercial software (SpecsLab Prodigy; Specs GmbH, Berlin). The XP core level peaks are deconvoluted with a mixed Gaussian – Lorentzian function after a Shirley background subtraction. Novacron Ruby S-3B and Remazol Brilliant Blue R dyes have been characterized after being drop casted. Each dye was dissolved in triple distilled water and dried on a glass substrate, which had a coating of Indium-Tin Oxide (ITO) on its surface. The coating offered electrical conductivity to the substrate, reducing the chances of electrical charging occurring when measuring the samples.

2.3.4. UV-Vis and Fluorescence spectroscopy

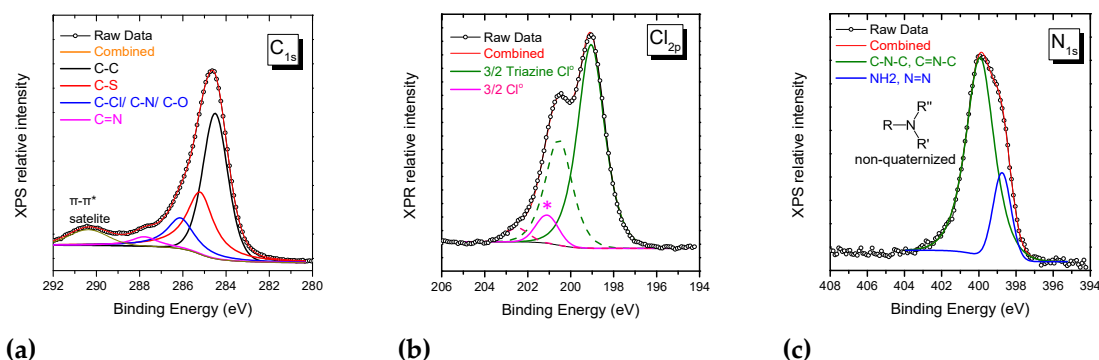
The interaction of dye-polymer binary systems in aqueous solution was studied by UV-Vis spectroscopy using a Hitachi U-3000 spectrophotometer (Hitachi High-Technologies Europe GmbH, Mannheim, Germany). All UV-Vis measurements were performed in air using quartz cuvettes. Fluorescence measurements were obtained by a Cary Eclipse Fluorescence Spectrophotometer G9800A (Agilent Technologies, Burlington, VT, USA). Excitation was set at 240 nm and collection was at 90° from a cuvette filled with the aqueous solution of the binary mixture that has been stirred for few minutes. Both UV-Vis and fluorescence measurements were performed in air using quartz cuvettes.

3. Results and Discussion

3.1. Characterization of reactive dyes

The XPS spectra collected from Novacron Ruby S-3B reactive dye in the spectral range of C_{1s}, Cl_{2p}, N_{1s}, Na_{1s} and S_{2p} orbitals are shown in Fig. 1. The C_{1s} spectral region may be fitted using three major peaks: (i) one attributed to C atoms participating in the benzene/naphthalene rings (284.5 eV), (ii) a second peak attributed to the C-S bond (285.2 eV) and (iii) a third one associated with C atoms attached to the quaternary nitrogen atom, the O atom or/and the Cl^o atom (286.2 eV) [36-38]. The N_{1s} spectral region can be fitted with two peaks of non-quaternized nitrogen atoms. The main peak is attributed to either C-N-C or/and C=N-C and is found at 400 eV, while the weaker one attributed to either NH₂ or N=N is observed at ~398.9 eV [37,38].

The sodium counterions are observed in the Na_{1s} spectral region (1071.9 eV), while in both Cl_{2p} and S_{2p} regions, doublets are recorded. The first doublet at ~199.0 eV is assigned to Cl^o attached to the triazine ring, while in the sulfur 2p spectral region a twin doublet is assigned to -SO₂-/SO₃⁻ contribution at 168 eV and to SO₄ at 169.2 eV [14,15]; the intensity ratio of the two peaks is ~4/1, in close agreement with the chemical structure of the dye, Fig. 1(f).



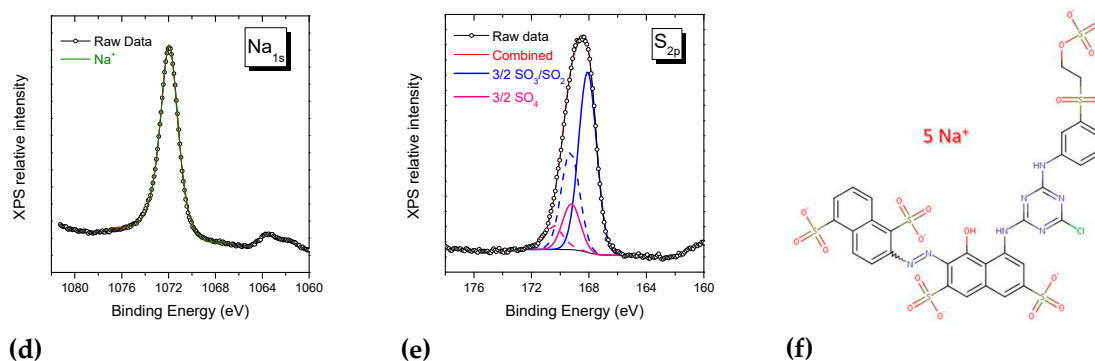


Figure 1. XPS spectra of Novacron Ruby S-3B in the spectral region of: (a) C_{1s} , (b) Cl_{2p} , (c) N_{1s} , (d) Na_{1s} and (e) S_{2p} . The molecular structure of the reactive dye is given in (f). The doublet of weak Cl peaks in (b) denoted by * had to be included in the fitting and may be explained as in reference [41].

XPS spectra of Remazol Brilliant Blue R reactive dye of C_{1s} , S_{2p} , N_{1s} , Na_{1s} , and O_{1s} orbitals' characteristic spectral regions are shown in Fig. 2. For this dye, as for the previous one, the stoichiometry derived from peak intensity ratios is close to the corresponding structure at molecular level. Notice that there is no signal in the Cl_{2p} spectral region and for the S_{2p} doublets the intensity ratio of the $-SO_2-/SO_3^-$ to $-SO_4^-$ species is $\sim 2/1$, in agreement with the structure given in Fig. 2(f).

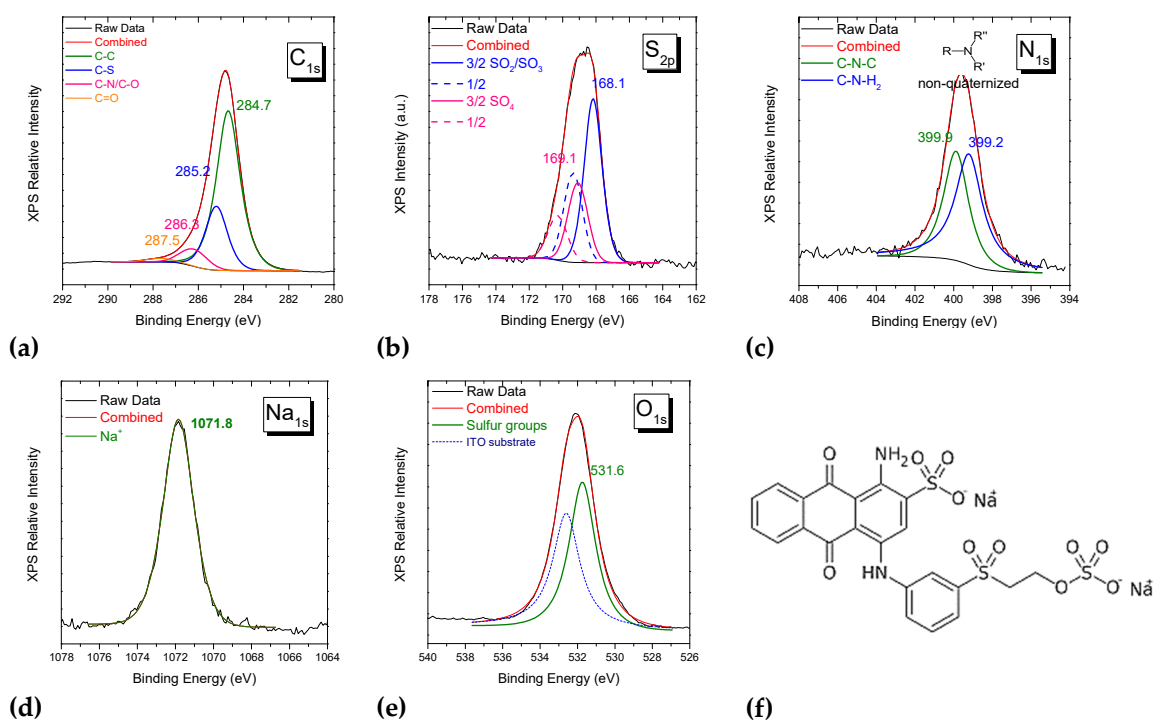


Figure 2. XPS spectra of Remazol Brilliant Blue R in the spectral region of: (a) C_{1s} , (b) S_{2p} , (c) N_{1s} , (d) Na_{1s} and (e) O_{1s} . The molecular structure of the reactive dye is given in (f).

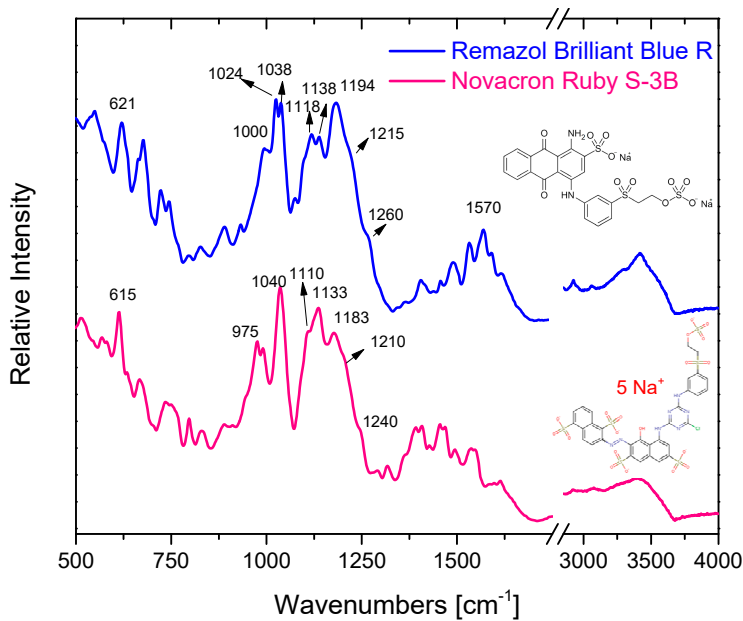


Figure 3. ATR-FTIR spectra of the reactive dyes Novacron Ruby S-3B and Remazol Brilliant Blue R.

The characteristic ATR-FTIR vibrational bands of both reactive dyes in the solid phase can be identified in Fig. 3. The spectral contribution of major structural groups, such as benzene/naphthalene/anthraquinone rings, chloro-triazine and sulfone/sulfonate/sulfate are found in the 950-1650 cm⁻¹ region; the most characteristic of them are listed in Table 2.

The bands at 1040 cm⁻¹ and 1183 cm⁻¹ (1038 cm⁻¹ and 1194 cm⁻¹ for Remazol Brilliant Blue R) can be assigned as symmetric and antisymmetric stretching vibration of the sulfonate (SO₃⁻) group, respectively. In the same manner, the symmetric stretching vibration of O=S=O group, which can be found separated or/and in the sulfate SO₄⁻ group, is found at 1110 cm⁻¹, while the antisymmetric one at 1210 cm⁻¹ (1118 cm⁻¹ and 1215 cm⁻¹ for Remazol Brilliant Blue R).

Table 1. This is a table. Tables should be placed in the main text near to the first time they are cited.

Ruby	Blue	Assignment
975m	~1000m	ring bending [42]
1040s	1038s	sym νSO ₃ + νCC [47,48]
1110m-sh	1118m-sh	sym SO ₂ str (of SO ₄ gr) [42]
1133m-s	1138m-s	Sym SO ₂ str of C-SO ₂ -C
1183s	1194sh	νCS + νCC + νsSO ₃ [47-51]
1210sh	1215s	SO ₃ asym str [47-51]
1280sh-m	1265sh	Asym SO ₂ str (of SO ₄ gr) [42]
1414w	-	C-N str [42]
1615m	1615m	C=N triazine ring str [42]
		Ring str [42]

3.2. Interaction between the cationic modifiers and the reactive dyes

3.2.1. Investigation of dye-polymer aqueous solutions through UV-Vis and fluorescence spectroscopy

Intermolecular interactions may affect the electronic properties of the molecular moieties with an apparent alteration of their optical absorption as well as fluorescence spectra. Both reactive dyes used in the current study contain anionic SO₃⁻ and SO₄⁻ groups, able to interact electrostatically with the cationic VBCTEAM units of the polymers. The dye with the most available interactive sites with the VBCTEAM units of the polymers is Novacron Ruby S-3B; 5 sites versus 2 for the case of Remazol

Brilliant Blue R. However, for all dye-polymer combinations homogeneous solutions were obtained for sufficiently low D/P^+ charge ratios. Therefore, we have chosen a fixed charge ratio for all binary systems, $D/P^+ = 1/5$, (the nominal dye negatively charged sites equal 20% of the cationic polymer sites). The absorbance and fluorescence spectra were recorded from these solutions and compared with the respective spectra of the solutions of the individual constituents.

Figure 4a depicts the UV-Vis spectra of aqueous solutions of PVBCTEAM, Novacron Ruby S-3B dye and the respective binary system with $D/P^+ = 1/5$. The polymer absorption bands at 224 and 261 nm are only hardly resolved in the binary system spectra. Concerning the absorption bands of the dye, these are shifted to higher wavelengths in the binary system; depending on the transition, this red-shift varies (2-15 nm), having a greater value for the $n-\pi^*$ type of transition(s) observed at ~500-550 nm. Alterations in the relative intensity of the bands can be resolved; however, they are not significant. Respective spectra were acquired for all dye-polymer combinations. Similar trends were noticed in all cases.

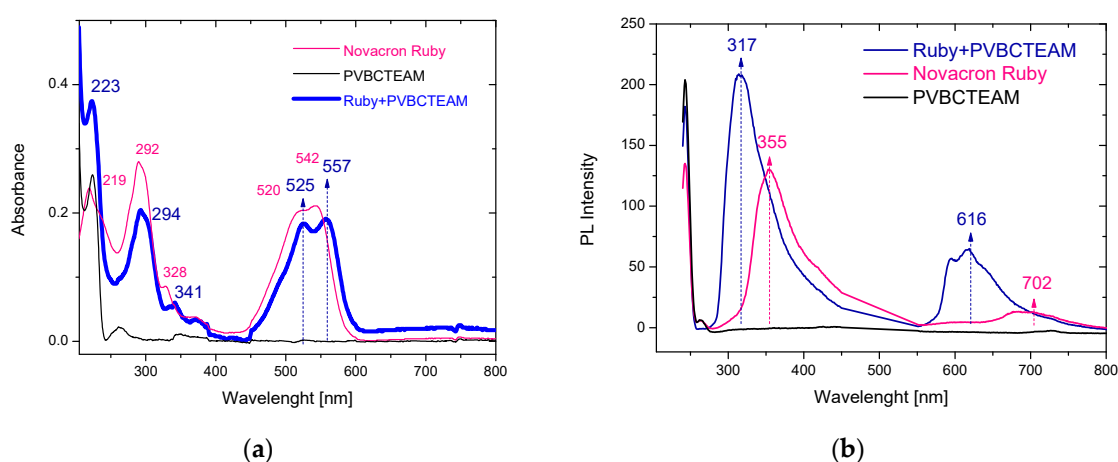


Figure 4. UV-Vis (a) and fluorescence (b) spectra of aqueous solutions of PVBCTEAM, Novacron Ruby S-3B and their binary system.

In agreement with the absorption spectra, the fluorescence spectra (Fig. 4b) of the corresponding systems exhibit spectral shifts as well. In this case, however, blue-shifts are observed along with considerable intensity increase. Hence, shifts in the range of 35-90 nm are observed in the binary system of Novacron Ruby S-3B and PVBCTEAM along with an intensity increase of the fluorescent peaks by ~65%. Similar observations were noticed for all dye-polymer combinations.

3.2.2. Investigation of dye-polymer precipitates through ATR-FTIR spectroscopy

From the previous discussion, it is evident that the electronic properties of the binary mixture deviate from those of the dye itself, which in turn suggests that any relevant experimental technique will in principle indicate the existence of the interaction between the reactive dye and the cationic polymer. Alterations in the respective vibrational modes may exist as well. To perform vibrational studies, such as ATR-FTIR spectroscopy, solid samples were obtained through setting the mixing dye/polymer charge ratio, D/P^+ , equal to unity. Under these conditions, as mentioned, a colored solid precipitate is formed, readily recovered through filtration.

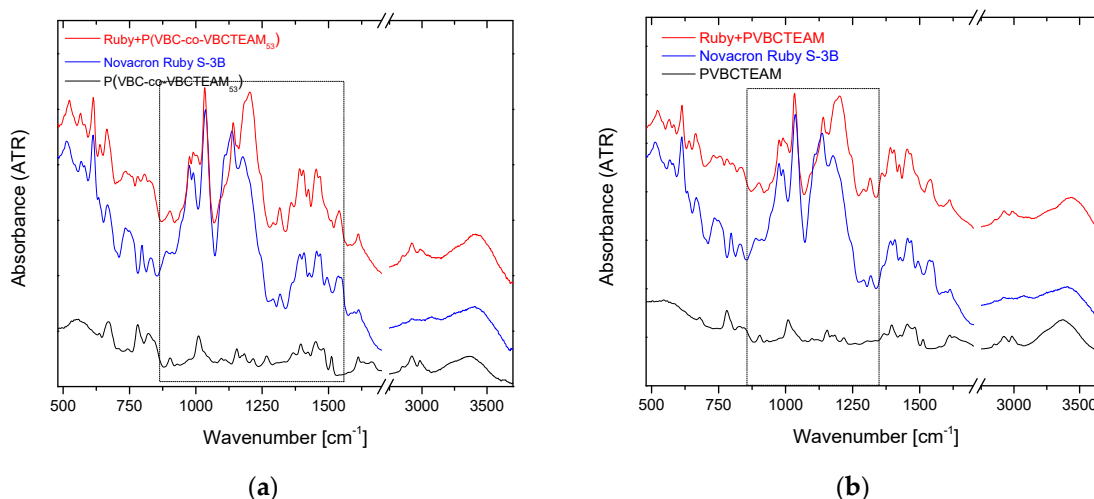


Figure 5. ATR-FTIR spectra of the dye-polymer precipitate of the binary systems of (a) P(VBC-co-VBCTEAM53) and (b) PVBCTEAM with Novacron Ruby S-3B. The spectra of the constituents are also given for comparison.

Figure 5(a) shows the ATR-FTIR spectra of the Novacron Ruby S-3B reactive dye, the cationic polymer P(VBC-co-VBCTEAM53) and their binary system, all in the solid state. The spectra are rather complicated; however, the bands in the 1400-1500 cm^{-1} spectral range, are attributed to benzene/naphthalene and triazine ring deformations. Since these modes are expected to be less affected by the intermolecular interactions with the cationic polymer (at least comparing to the vibrational modes attributed to the anionic sites of the reactive dyes), these bands were considered as reference bands. After the normalization of the spectra, the most interesting changes are the relative intensity of the symmetric stretching vibrations of SO_3^- (1040 cm^{-1}) and SO_4^- (1110 cm^{-1}) with respect to the asymmetric ones (1183 cm^{-1} and 1205 cm^{-1}) observed in detail in Fig. 6(a). Similar results were obtained for the binary system of NR-homo, Fig. 5(b) and Fig. 6(b).

Identical spectral behavior can be observed referring to the P(VBC-co-VBCTEAM53) or PVBCTEAM and Remazol Brilliant Blue R precipitate (Fig. 7). Both intensities of the symmetric stretching vibrations of SO_3^- and SO_4^- groups have decreased (1038 cm^{-1} and 1120 cm^{-1} , respectively), with respect to the intensity of the asymmetric vibrations at 1194 cm^{-1} and 1215 cm^{-1} .

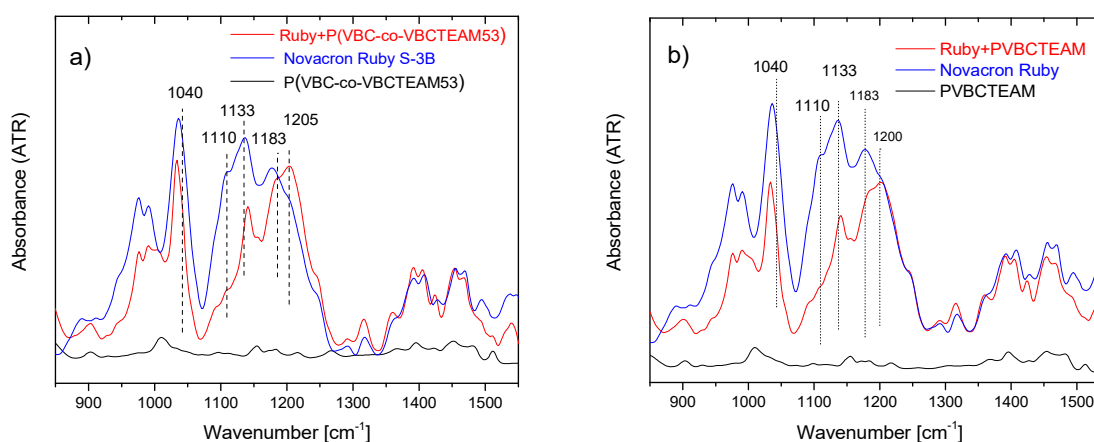


Figure 6. Detailed ATR-FTIR spectra of the dye-polymer precipitate of the binary systems of (a) P(VBC-co-VBCTEAM53) and (b) PVBCTEAM with Novacron Ruby S-3B in the 900-1500 cm^{-1} spectral region. The spectra of the constituents are also given for comparison.

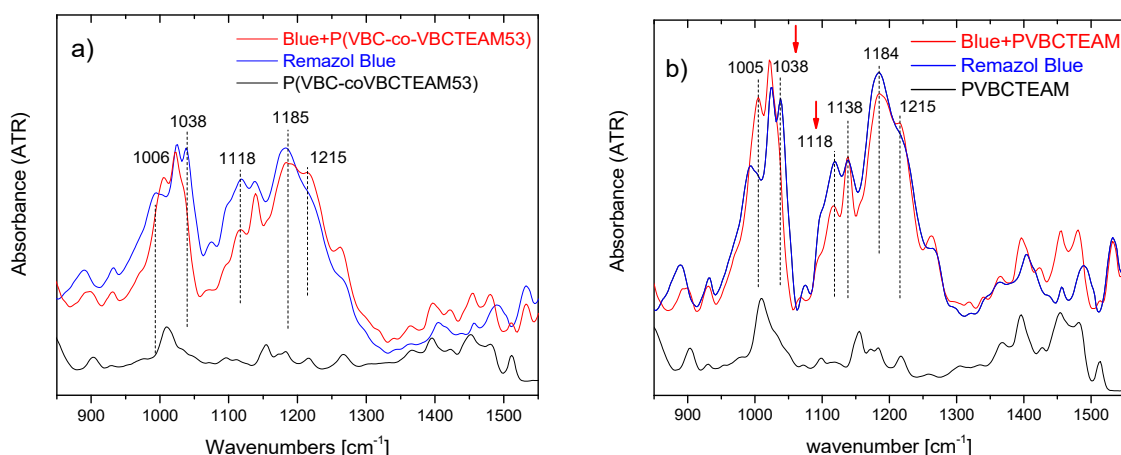


Figure 7. ATR-FTIR spectra of the dye-polymer precipitate of the binary systems of (a) P(VBC-co-VBCTEAM53) and (b) PVBCTEAM with Remazol Brilliant Blue R. The spectra of the constituents are also given for comparison.

All these spectral differentiations may lead to the early conclusion that changes happen in the counterion of the sulfate/sulfonate anionic groups of the dye molecules. The Na^+ counterions of the dyes probably have been replaced by the quaternary N^+ groups of VBCTEAM units of the polymers; the latter induces changes in symmetry of these sulfate/sulfonate species affecting their vibrational behavior.

The work of Shishlov and Khursan [52] focuses on the comparison between experimental and calculated vibrational spectra of benzenesulfonate salts, which are molecular units similar to some of the most characteristic ones of the reactive dyes in the current work; therefore, their findings may be applied on the study of pristine dyes and their binary system with cationic polymers. The authors stated that bidentate species introduce splitting of the asymmetric SO_3^- vibrational band with the two generated modes well separated by $>150 \text{ cm}^{-1}$. On the contrary, in more symmetric species, such as tridentate or dimers, the corresponding splitting is not so profound. The authors also described that for the organic sulfonic species, the coordination of sulfate/sulfonate ions with cationic counterparts is complex and depends on the environment. Considering the complexity of the dye molecules and their FTIR spectra it is ambiguous to explain the spectral alterations; Nevertheless, it is evident that the interaction of the reactive dyes with the cationic polymers involves exchange of the cationic counterpart Na^+ with the quaternary N^+ groups of VBCTEAM units, which in turn critically affects the symmetry of the sulfate/sulfonate species.

3.2.3. Investigation of dye-polymer precipitates through XPS spectroscopy

The estimation of the ratio between the species of dyes and the VBCTEAM units in the solid precipitates is of importance since it evaluates the number of dye molecules that each polymeric chain can uptake. This factor is not straightforward, and it is critical in terms of both scientific knowledge and applications since each dye possesses different active sites and may pose specific steric hindrances when interacting with the polymer chains.

The solid precipitates obtained at a mixing dye/polymer charge ratio fixed at $\text{D}/\text{P}^+=1$ were investigated through XPS spectroscopy. Fig. 8 depicts the N_{1s} spectral region of the XPS spectrum of the NR-copo precipitate. The accumulated spectrum consists of bands assigned to both quaternary and non-quaternary nitrogen atoms. The non-quaternary nitrogen contribution at 399.5 eV is attributed to the dye Novacron Ruby S-3B, a band that is well separated from the respective one of the quaternized nitrogen of VBCTEAM units located at a binding energy of 402 eV. This separation can be useful not only for qualitative but also for quantitative analysis in case of binary system study or/and the study of dyed cotton (see section 3.3). Regarding this particular binary system, an almost equal amount of nitrogen contribution can be detected ($\text{N}^+/\text{N} \sim 1.2/1$). Considering that this dye contains 7 nitrogen atoms, whereas VBCTEAM unit contains only 1 nitrogen atom, this result

indicates a ratio of 1 Novacron Ruby S-3B dye molecule for every ~ 5.8 VBCTEAM units, namely close to stoichiometric charge ratio, since the dye contains 5 negatively charged units. The same ratio value was estimated for the binary system of the same dye with PVBCTEAM (NR-homo) after calculation of the corresponding intensity ratio in the spectrum shown in Fig. 2S.

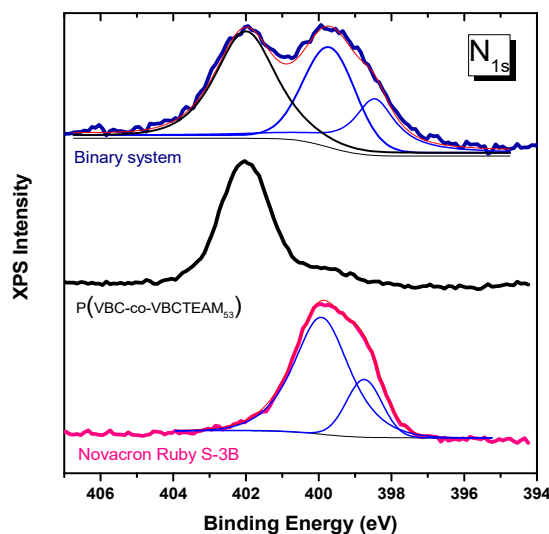


Figure 8. XPS spectra of Nitrogen orbital 1s for the copolymer, the dye Novacron Ruby S-3B and the binary system.

Sulfonates (SO_3^-) and sulfate (SO_4^-) of the Novacron Ruby S-3B molecule in Fig. 9(a) have some noticeable differences when compared to the corresponding spectrum of Remazol Brilliant Blue R binary system. These slight changes are attributed to the differentiation of the chemical environment of the anionic groups, after the electrostatic interaction. In this direction, 0.2-0.3eV increase at FWHM of the overall sulfur peak can be justified, while the peak position remains constant. These changes are mainly found in the Novacron Ruby S-3B system that contains four sulfonate groups, in which some of them may not interact due to steric hindrance.

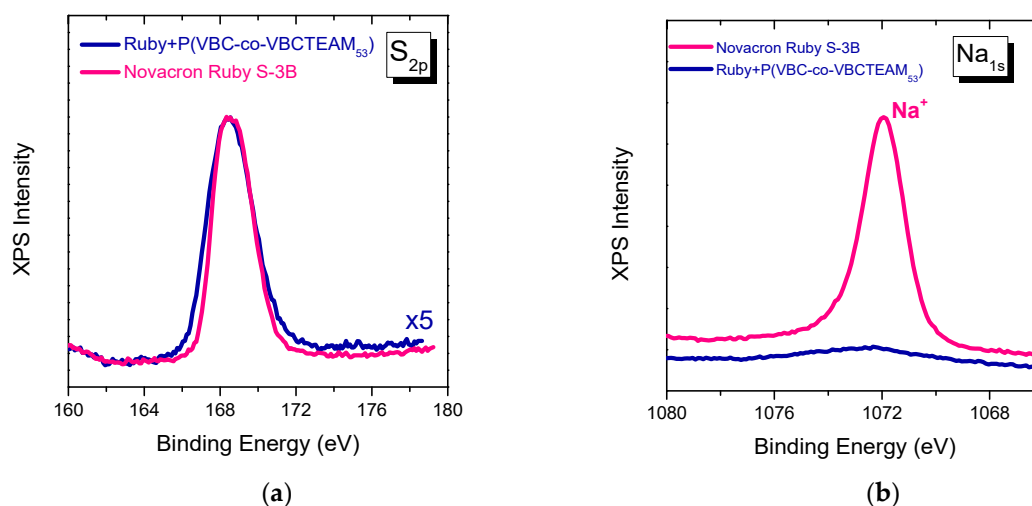


Figure 9. XPS spectra of Sodium orbital 1s (a) and Sulfur 2p (b) for Novacron Ruby S-3B dye and the binary system.

The sodium 1s orbital peak at 1072 eV, in Fig. 9(b), is particularly strong in the Novacron Ruby S-3B spectrum indicating the counterions of the existing five anionic sites, while it is very weak in the case of the binary system.

In the chlorine 2p orbital peak at Fig. 10, there is a multiple contribution of chlorines Cl^0 of both the Novacron Ruby S-3B dye (199 eV) and VBC units for the case of the cationic copolymer (200 eV), while the chlorine counterions Cl^- of VBCTEAM units are observed at 197 eV. In the case of the binary system the Cl^- contribution is severely depressed.

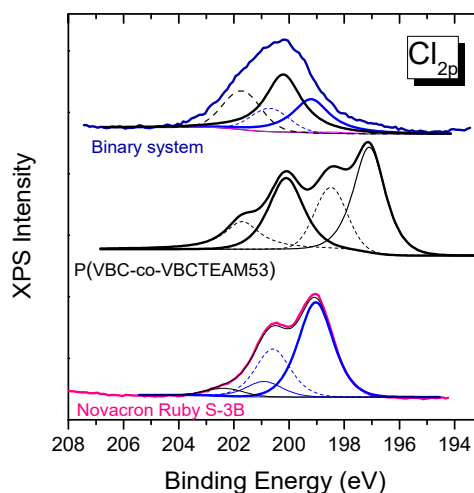


Figure 10. XPS spectra of the chlorine orbital 2p for the copolymer, the Novacron Ruby S-3B dye and the dye-polymer precipitate.

This disappearance of both sodium (dye) and chlorine (polymer) counterions, indicate the strong tendency for the cationic polymer to interact with the reactive dye through electrostatic interactions. The replacement of Na^+ ions with the cationic units of the polymer in the binary system is in agreement with the ATR-FTIR spectroscopic results that indicate alterations in the local environment of the sulfonate/sulfate groups.

The same arguments hold for all the different binary systems studied. It is interesting to note that for the case of Remazol Brilliant Blue R, from the respective spectra of Fig. 2S it is calculated that the ratio of VBCTEAM units per dye molecule is ~ 3.5 when binding with PVBCTEAM, and ~ 2 when binding with P(VBC-co-TEAM53). The lower ratio values for Remazol Brilliant Blue R, compared to the respective values for Novacron Ruby S-3B, can be explained by the different number of anions in their structure (2 for Remazol Brilliant Blue R and 5 for Novacron Ruby S-3B) as well as by the difference in size of the dye molecules.

3.3. Role of the cationic modifier in the dyeing process of cotton

The general reaction mechanism of reactive dyes with unmodified cellulose surface consists of two major steps. First, the physical contact of the molecules through the sorption of dyes from the dye bath on the cotton fiber and second, the chemical reaction with the cellulose. The reaction proceeds only in the presence of an alkaline bath which is used to activate the cellulose reactive site (fixation phase) [33,34]. Vinyl sulfone is the reactive group of both dyes used in the present study. In fact, during the dyeing process, the masking sulfate group is removed by a 1,2-trans elimination reaction, to form the free vinyl sulfone group, able to react with fiber nucleophiles by the Michael addition reaction [33]. Vinyl sulfone dyes are applicable at the range of 40-60 °C [35]. Novacron Ruby NRS-3B is bifunctional, since it contains also a chloro-triazine reactive site, able to react with cellulose through the classical $\text{S}_{\text{N}}2$ bimolecular substitution from nucleophilic attack of the electron-rich oxygen in the cellulosate anion on electron deficient carbon atoms in the triazine heterocycle (chlorine leaving group). The most important disadvantage of this dye category is the increased requirement of alkaline concentration (sodium carbonate) and temperature (80 °C) in the dye bath [33-35].

When investigating the role of cationic modification of cotton, it is necessary to understand the effect on increasing the retention of dye. To demonstrate the capabilities of cotton modification with the present cationic modifiers, we applied the same dyeing protocols on modified and unmodified fabrics. The protocol involved high and low temperatures with and without salt (Section S2). Cationization resulted in fibers characterized by a thin modified layer. The thickness of the modified layer is so small that spectroscopic techniques such as FTIR and Raman scattering with a penetration depth of very few microns offer marginal information and extremely sensitive surface techniques, such as XPS, could identify and provide insight of the physical chemistry associated with the modification process. This argument is also supported by Scanning Electron Microscopy images (Image S1), where the morphology of untreated, dyed untreated and dyed treated fibers remains similar in the scale of hundred nm. This observation indicates that both modifier and dye are covering just a few nm of the fibers' surface, which is similar to the order of XPS penetration depth.

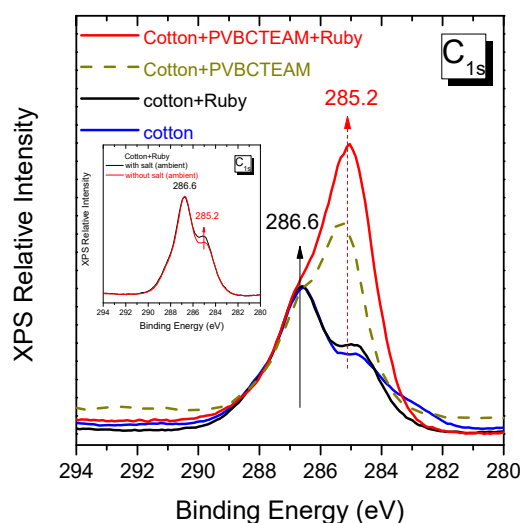


Figure 11. XPS spectra of carbon orbital 1s of the untreated fabric substrate, low temperature dyed cotton fabric (Novacron Ruby S-3B), modified fabric with PVBCTEAM and low temperature dyed modified fabric. Inset: low temperature dyed fabric with and without adding salt in the dyeing bath.

The quantity of dye retained on the cellulose fibers' surface can be qualitatively extracted by XPS and more clearly in the carbon 1s spectral region. XPS spectra obtained from the samples after the dyeing process (using Novacron Ruby S-3B) in this particular spectral region can be seen in Fig. 11. The most characteristic peak of cotton is the one at 286.6 eV; we use this peak as an internal standard in order to semi-quantify the degree of modification as well as of dyeing, taking into account that both modifier and dyes exhibit a characteristic band at ~285 eV. We thus observe a small intensity increase of the latter band after dyeing unmodified cotton at ambient temperatures. This small intensity increase agrees well with the macroscopic poor fabric color intensity (Image 1), while similar color intensity is observed in the modified fabrics with the copolymer. Modified fabrics exhibit strong contribution in the ~285 eV band indicating grafting of the cationic polymer to the cellulose fibers, while subsequent dyeing of the modified fabric resulted in further increase of the same band intensity. The ability of the XPS to semi-quantify the quantity of dye on fabrics may be furthermore demonstrated in the inset of Figure 10 where small differentiation of the 285 eV intensity is resolved for fabrics dyed with and without salt at ambient temperatures, the first of which were characterized by slightly better retention of dye.

The ability of this surface technique further demonstrates the potential of the cationic modification process to retain large quantities of dye (more than an order of magnitude compared to the unmodified cotton) even at low temperatures. The higher degree of dyeability caused by the presence of the cationic modifier on the cotton surface is clearly resolved in Image 1. Unmodified fabrics dyed using the typical procedure with and without salt exhibit low dyeability at low

temperatures; the presence of salt results in a slightly higher dyeability. In comparison, modified fabrics exhibit high dyeability at low temperatures even without the presence of salt. Apart from being more vivid, the color on these fabrics is also particularly uniform. Extensive colorimetric studies performed on dyed fabrics modified by a series of cationic modifiers similar to the ones used in the current study can be found in [53]. In the next paragraphs, the XPS study of the pair of dyed fabrics depicted in Image 1 will be given as a case study. The results of all other possibilities are comparable and lead to the same conclusions.

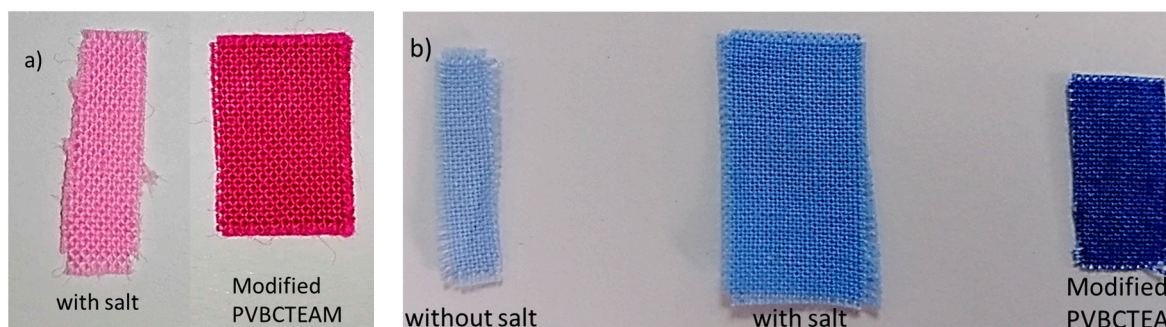


Image 1. Dyed cotton fabric at low temperatures with: a) Novacron Ruby S-3B and b) Remazol Brilliant Blue R. Comparison of the color intensity for samples with and without modification is unambiguous. For the modified fabrics the dyeing protocol without salt (S2.1) was followed.

The N_{1s} spectral region in the XPS spectra can be used to verify the coexistence of the components (quaternary VBCTEAM units and non-quaternary species of dyes), while the Cl_{2p} one to reveal the interactions involved between cellulose, cationic polymer and dye.

The nitrogen existing in the dyed fabric is a combination of cotton residues and dye, as indicated by the peak at ~ 400 eV in the N_{1s} spectral region of the XPS spectra (Fig. 12a); the cotton residues contribution is considered much less than that of the dye. For the case of modified dyed fabrics two peaks are resolved, at ~ 400 eV assigned mainly to the dye and the ~ 402 eV assigned to the VBCTEAM units. From the signal to noise ratio, it is clear that the dye retention is significantly increased after treatment, in agreement with the respective findings from the carbon 1s spectral region.

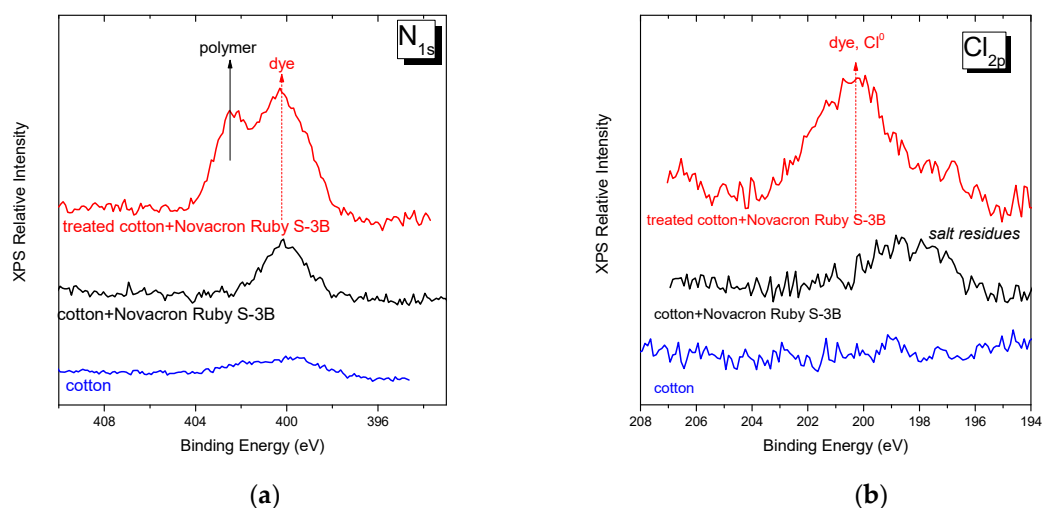


Figure 12. XPS spectra of (a) nitrogen orbital 1s and (b) chlorine 2p orbital for untreated cotton fabric, untreated dyed cotton and modified dyed cotton fabric with Novacron Ruby S-3B dye.

The Cl_{2p} spectral region, Fig. 12(b), is indicative of the chloro-triazine sites when dyeing with the Novacron Ruby S-3B dye (at ~ 199 eV). This chemical unit is one of the two sites of potential direct interaction of this particular dye molecule with cotton. In the same spectral region, the Cl atoms of

the polymers containing VBC units also contribute (~ 200 eV). However, as already shown [32], their contribution in the modified fabrics cannot be observed in the XPS spectra; the latter was explained as an indication of polymer grafting on cellulose through this reactive site. Finally, the Cl_{2p} spectral region is characteristic of Cl^- at ~ 198 eV.

Our results reveal that no Cl_{2p} bands are observed in the fabric, nor in the unmodified dyed fabric. The latter may be explained either by the low quantities of dye molecules retained at low temperature processes and/or by the direct grafting of the dye to cellulose. The weak band of chlorine ions observed (at ~ 197 eV) in the spectra of unmodified fabric are possibly attributed to small salt residues after the dyeing process performed in alkaline 1M NaCl solutions. The clearly resolved neutral chlorine band observed in the spectra of modified-dyed fabrics suggests a considerable fraction of unreacted dye sites. In the same spectra, the Cl^- ion contribution is minimal and may explained either to salt residues or as a small number of counterions to the cationic VBCTEAM units that did not interact with dye molecules.

The question of whether the typical reactive dye process of grafting on cellulose i.e. through vinyl sulfone and chlorine sites is participating in the dyeing process of modified fabrics is difficult to be answered. As explained above, for Novacron Ruby S-3B dye it appears that its reaction with cellulose is not fully performed (Cl band intensity in Fig. 11b). As far as the masking sulfate groups are concerned, the XPS sulfur spectral region, which in principle offers the ability to extract the information, requires fitting of the respective band with two bands (namely SO_3^- and SO_4^- groups), a difficult task, especially for spectra of low signal to noise ratio. Observation of the width of the band for the untreated dyed fabric (Fig. 13) indicates that there exists a narrowing of the band-width (FWHM=2.3) if compared to the pristine dye band (FWHM=2.7). The XPS spectrum of pristine Novacron Ruby S-3B dye can be fitted with two doublets in the S_{2p} spectral region as shown in Fig. 1e. For the unmodified dyed cotton, a fitting is satisfactory by incorporating only the SO_3^- pair of peaks (main peak at 168 eV) indicating a consumption of the SO_4^- species during the dyeing process of cotton. The spectra of pristine Novacron Ruby S-2Band the modified-dyed cotton are compared in the Inset of Fig. 12. The similarity in the peak profiles and peak widths suggests that the SO_4^- site are still present, suggesting that the dye has not been bonded to cellulose through the vinyl sulfone mechanism.

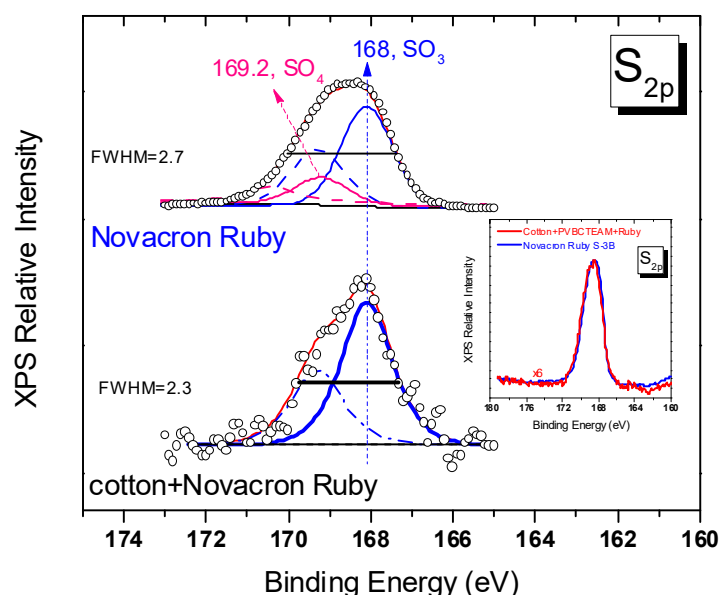


Figure 13. Fitted XPS spectra for the sulfur orbital 2p of pristine Novacron Ruby S-3B and untreated dyed cotton. Blue peaks denote the SO_3^- doublet while pink curves denote the contribution of the SO_4^- doublet (absent in the untreated dyed cotton). Inset demonstrates the similarity of the spectra between pristine Novacron Ruby S-3B and the modified dyed cotton.

4. Conclusions

The role of cationic modification of cotton fabric with P(VBC-co-VBCTEAM_x) polymers during the dyeing process is explored in the present work at molecular scale. Several spectroscopic techniques were applied, and detailed information related to the interaction of the reactive dye molecules with the cationic polymer modifiers at molecular level was acquired. Two differently structured reactive dyes were used: (a) Novacron Ruby S-3B possessing five negatively charged sulfonate/sulfate groups and two possible reactive sites with cellulose (vinyl sulfone and chlorotriazine) and (b) Remazol Brilliant Blue R possessing two negatively charged sulfonate/sulfate groups and one possible reactive site with cellulose (vinyl sulfone). Regarding the number of available cationic sites in the modifier its effect was investigated by using the two extreme values for the cationic content x that secure solubility in water ($x=53$ and $x=100$). Binary dye-polymer aqueous solutions (when polymer is in large excess) as well as precipitates (at stoichiometric charge ratio) were studied. UV-Vis spectroscopy indicates dye-polymer interactions in the aqueous solutions of the binary systems by measurable small red-shifts in the dye absorption bands. In addition, noticeable blue shifts in the dye bands are observed in analogous fluorescence experiments. In the precipitates of the binary systems, experimental evidence for the coupling of sulfonate/sulfate anions with N^+ is provided by ATR-FTIR and XPS spectroscopy. Furthermore, XPS enabled the extraction of the ratio of the number of VBCTEAM units per one dye molecule for each of the binary systems studied. Finally, for the modified dyed fabrics, XPS indicates a considerable portion of sulfate and chlorotriazine dye reactive sites, which indicates that the main mechanism of dye molecules attached to the fiber is through dye-modifier electrostatic interactions. As a result, the cationic modifier containing both VBC and VBCTEAM units acts as a connecting linkage of cellulose and dye molecule. Understanding the different interactions involved in the proposed dyeing process may assist in the upscaling and optimization of the process as well as give insight for alternative structures of polymer chains that offer additional properties to the modified cotton fabrics. Furthermore, it triggers additional research required to justify the problem of dye release during fabric washing while exploitation of applying the use of the proposed modifiers with other non-reactive dyes may be also reasonable.

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