Electrokinetic Phenomena of Cationised Cotton and its Dyeability with Reactive Dyes


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Abstract

Interface phenomena have a significant role in the wet finishing processes. Therefore in this paper the electrokinetic phenomena of cotton fabric cationised with a commercial cationic compound were researched. After cationisation, characterisation of the surface and chemical composition was performed by FTIR-ATR. Electrokinetic phenomena - Zeta potential, Isoelectric point (IEP) and Point of zero charge (PZC), were determined according to the streaming current/streaming potential method and a specific amount of surface charge according to the back-titration method. The affinity of such modified cotton to reactive dye-stuff of different functional groups was investigated through the K/S values. The influence of electrolyte addition to the dye bath was investigated as well.

Key words: cotton, cationization, electrokinetic phenomena, reactive dyeing.

Introduction

In textile wet finishing processes electrokinetic phenomena (zeta potential, electrokinetic surface charge of textile material) and the strength of fibre bonds play an important role.

The electrokinetic (zeta, ζ) potential is part of the total potential drop occurring in the intermediate surface layer at the boundary of the solid/liquid phases as a consequence of the ion distribution from the solid surface to the liquid mass [1]. At the interface of electrically charged textile fibres and an aqueous solution of electrolyte, surfactants or dyes electric double layer is set up. Moving one of these two charged surfaces results in electrokinetic (zeta) potential.

In Figure 1 [2] it is important to notice the imaginary plane at distance d from the solid surface which presents the border between the layer of charges attached to the solid surface (Stern layer) and diffusively distributed charges extending toward the liquid bulk (Gouy-Chapman layer). Plane β at distance 0 < β ≤ d is known as the inner Helmholtz plane (IHP). At distance d or the outer Helmholtz plane (OHP) the ions attached due to Coulombic forces are distributed. Correspondingly Ψ₀, Ψ β and Ψ d are the surface potential, σ₀, σ β and σ d - surface charges, IHP - the potential and diffuse layer potential (Stern or OHP potential). The charge balance and sequence of potentials of the whole system should be [3]:

\[ \sigma_{0} + \sigma_{β} + \sigma_{d} = 0 \]  
\[ \Psi_{0} > \Psi_{β} \geq \Psi_{d} \geq \zeta \]  

Finally the net surface charge σ₀ can be calculated according to the Gouy-Chapman model [3]

\[ \sigma_{0} = -\sigma_{d} = \sqrt{8RT\epsilon_{0}} \sinh\frac{F\Psi_{d}}{2RT} \]  

There are few zeta potential measurement principles like electrophoresis, sedimentation potential, electro osmosis, streaming potential/current, potential of colloidal vibration, and the electrokinetic sound amplitude [4, 5]. In most cases the method of measuring current/streaming potential or electro osmosis is used for fibres, whereas electrophoresis is used for dyes [2, 5 - 8]. It should be pointed out that different measuring methods result in different values of zeta potential under identical conditions. On the other hand, the isolectric point (IEP), the concentration value of potential - determining ions where the zeta potential is zero, is the parameter which gives an insight into the character of the test material [2, 3]. Generally for Brönstead acids and bases, IEP is the pH value at which \( \zeta = 0 \) (pH_{IEP}). Another electrokinetic parameter is the point of zero charge (PZC), representing the amount of opposite charged ionic surfactant added to electrolyte adsorbed to the surface for reaching a zeta potential equal to zero [2, 3].

Figure 1. Models of a) the electrical interfacial layer and development of interfacial potential, b) surface cationised by the surfactant and development of interfacial potential [2].
Electrokinetic phenomena give information about the nature and dissociation of functional groups, the hydrophilicity or hydrophobicity of the fibre surface as well as about ions or water sorption. Fibre sorption properties are influenced by the molecular (chemical structure, molecular mass, number of functional groups) as well as supramolecular structure of fibre (molecular orientation, degree of crystallinity, crystallite dimensions, portion of amorphous regions, size and shape of voids etc.). A significant influence on the sorption properties of fibres is the amount of accessible groups (hydroxyl, carboxyl, sulfate and amino groups) and the portion of amorphous regions where the adsorption processes take place [6]. The change in the number of functional fibre surface groups, e.g. by blocking in the dyeing and finishing processes, and their dissociation affect the distribution of the surface charge, causing changes in the thickness and distribution of the electric double layer, which results in different fabric electrokinetic phenomena [6].

Immersed in water (pH 6.5 - 7.0) textile fibres show negative values of the \( \zeta \)-potential (-10 mV to -60 mV) and negative surface charge, because chemical functional groups dissociate in water, giving off or absorbing anions [4, 6 - 8]. Therefore for cotton cellulose the adsorption processes of anionic substances are difficult due to repulsive forces between particles of the same electrical sign. During the mercerisation process the cotton unit cell changes from cellulose I to cellulose II, resulting in more energetically favorable material; but the repulsive forces are still present [7 - 9].

Reactive dyestuffs, which are used in more than 50% of cotton dyeing [10] due to the variety of brilliant shades, excellent color fastness and environmentally safety, in an alkaline medium are able to covalent a bond between carbon atoms in the dyestuff molecule and oxygen atoms in hydroxyl groups of cellulose [11]. The most common commercial systems involve vinyl sulphon (VS) and monochlorotriazine (MCT) reactive groups. The main problem in dyeing with reactive dyes is low affinity caused by existing repulsion forces between electronegative charges in both cellulose in cotton fibre and reactive dyestuff. To overcome these forces in dyeing processes, a large amount of electrolyte is needed, which is economically and ecologically unfavorable. On the other hand, during the dyeing process with reactive dyes, the dyestuff not only reacts with fibre but also with water as well, resulting in hydrolysed dyestuff which remains in the dyeing bath or exhausted on fibre, similar to direct dyestuff, endangering color fastness. To increase the degree of exhaustion and fixation of reactive dye and save electrolyte, physical and chemical modification of cellulose fibre procedures can be undertaken. Therefore alternative methods of cotton dyeing have been researched in recent years, one of which is cotton modification using amines and/or quaternary ammonium compounds, which is based on the etherification of cellulose in an alkaline medium by blocking the primary hydroxyl group of cotton cellulose with cationic compounds. Consequently cationised cotton shows a less negative or even positive electric charge on the fibre surface, which increases its affinity to anionic compounds [12 - 17]. The results of chemical, structural and morphological changes in cotton cellulose after treatment with triazine derivatives which contain anionic and cationic groups [15] and the effects of such treatment in reactive dyeing were recently published [16]. On modified cotton cellulose several phenomena were identified: forming of new molecular structures that contain cationic and anionic groups, decreases in the level of crystallinity and modification of the surface morphology. Modified cotton cellulose achieved a greater degree of exhaustion and fixation of reactive dyestuff than unmodified cellulose, as a result of newly formed groups [12 - 17]. Therefore it was of great interest to research electrokinetic phenomena of cotton fabric treated with a commercial cationic agent to improve the ability of cotton dyeing with reactive dyestuff of different functional groups.

### Experimental

#### Material

Plain weave bleached fabric of 100% cotton fibre was used. The mass per surface area is 204.5 g/m². A quaternised polylycol ether of fatty amine with a cationic character, Sintegal V7 conc. (Chemapol - Czech Republic) was applied in three concentrations (0.5 g/l, 1 g/l and 2 g/l) by the exhaustion method at 50 °C for 30 minutes. Then 10 g/l Na₂CO₃ was added and the treatment continued for another 30 minutes for the etherification of cellulose in the alkaline medium.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>Unmodified (bleached) cotton fabric</td>
</tr>
<tr>
<td>P0,5</td>
<td>Bleached cotton fabric treated with 0.5 g/l of cationic compound</td>
</tr>
<tr>
<td>P1</td>
<td>Bleached cotton fabric treated with 1 g/l of cationic compound</td>
</tr>
<tr>
<td>P2</td>
<td>Bleached cotton fabric treated with 2 g/l of cationic compound</td>
</tr>
</tbody>
</table>

Afterwards the cationised cotton fabrics were neutralised in 5% CH₃COOH, rinsed with distilled water and dried at room temperature. Table 1 shows the labels and treatments of cotton fabric.

#### Methods

The characterisation of the surface and chemical composition of cationised cotton fabrics was performed by Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) spectroscopy on a Spectrum GX FT-IR (Perkin-Elmer).

The electrokinetic potential was measured by the streaming potential/current method using a Brookhaven-Paar Electrokinetic Analyser (EKA) with a stamp cell and calculated according to the Helmholz-Smoluchowsky equation [5]:

\[
U_p = \frac{\zeta \cdot \epsilon \cdot e_0 \cdot Q \cdot R \cdot \Delta \rho}{\eta \cdot L} 
\]

\[
The Zeta potential was investigated versus pH and versus ionic surfactant addition. The isoelectric point (IEP) of the textile fabrics was determined as well as the point of zero charge (PZC) using N-cetylpyridinium chloride (N-CPC).

The specific quantity of the surface charge was calculated after the back titration method [6] by applying a Titirino 736 (Methrom) using ionic surfactant electrode 6.0507.120 (Methrom). N-CPC was used as a cationic, and sodium decyl sulphate (SDS) as an anionic surfactant polyelectrolyte solution. The specific amount of surface charge per 1 g of
The adsorption ability of reactive dyestuffs – monochlorotriazine Ostazin Red H-3B (CI Reactive Red 45) by Chemapol, Czech Republic, and vinylsulphone Remazol Red B (CI Reactive Red 22) by Dy Star, Germany, was determined after dyeing through K/S values using remission a SF 600 PLUS CT spectrophotometer (Datacolor). Dyeing was performed at a concentration of 1% owf reactive dyestuff with and without the addition of electrolyte (10 g/l and 50 g/l NaCl), LR 1:45, at 80 °C for Ostazin and 60 °C for Remazol, for 2 h, in Ahiba G7B (Datacolor). After rinsing it was dried at room temperature.

Color measurements were carried out on both sides of the sample to determine parameters for calculation of the color intensity (K/S), and the increment of color intensity (I) at λ = 550 nm for Ostazin Red H-3B and λ = 520 nm for Remazol Red B, using the Kubelka-Munk equation:

$$ I = \frac{K}{S} = \frac{(1-R)^2}{2R} $$

Table 2. Zeta potential (ζ), isoelectric point (IEP), point of zero charge (PZC) and specific amount of surface charge (q) of modified cotton fabrics.

<table>
<thead>
<tr>
<th>Fabric</th>
<th>ζ, mV at pH 10</th>
<th>IEP</th>
<th>PZC*, mg/l</th>
<th>q, C/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>-18.9</td>
<td>&lt;2.8</td>
<td>67.72</td>
<td>-2.2870</td>
</tr>
<tr>
<td>P0.5</td>
<td>-15.3</td>
<td>3.82</td>
<td>59.12</td>
<td>-0.1638</td>
</tr>
<tr>
<td>P1</td>
<td>-14.9</td>
<td>3.98</td>
<td>53.05</td>
<td>0.1998</td>
</tr>
<tr>
<td>P2</td>
<td>-13.7</td>
<td>4.34</td>
<td>49.94</td>
<td>0.2989</td>
</tr>
</tbody>
</table>

Results and discussion

Characterisation of the surface and chemical composition of cationised cotton fabrics were researched by FTIR-ATR analysis (Figure 2). In the fingerprint area (1450 cm⁻¹ to 850 cm⁻¹), characteristic ribbons appear on 1155 cm⁻¹, 1105 cm⁻¹, 1050 cm⁻¹, 1025 cm⁻¹, 1005 cm⁻¹, 985 cm⁻¹ and 895 cm⁻¹ for all fabrics. Even though cationisation occurred, change in the chemical composition of cotton cellulose did not. From IR spectrums it is evident that a significant change (detectable by IR) in chemical composition during the modification did not occur because all spectrum peaks are in the same position. On the other hand it is evident that the absorption of IR spectra is changed in cationisation. By applying a higher concentration of the cationic compound, absorption is higher.

Results of electrokinetic phenomena of the cotton fabrics (electrokinetic potential, isoelectric point (IEP), point of zero charge (PZC), specific quantity of surface charge) are presented in Table 2 and Figures 3 and 4.

As was said, the surface of textile fibres in neutral aqueous solutions is negatively charged due to the dissociation of functional groups, or specific ion adsorption of solution to the surface. The dissociation of surface acidic or basic functional groups which belong to a class of Bronstead acids and bases [3, 17] is probably the main source of surface charge, as shown by Equations 9 and 10.

FibAH +H₂O ➔ H₃O⁺ + FibA⁻ (9)
FibB + H₂O ➔ FibBH⁺ + OH⁻ (10)

where FibAH is an acidic surface functional group, such as –COOH, and FibB is a basic group, such as –NH₂. In the case of raw (untreated) cotton material hydroxyl and carboxylic groups exist, but they are covered by non-cellulose compounds. Scouring and bleaching processes make available and cause the formation of new surface groups (–CO, –CHO and –COOH) [7 - 9]. Since in this paper bleached cotton fabric (P0), which contains both hydroxyl and carboxyl groups, was used, it can be described as Bronstead acid eq. (10). It has a low zeta potential (ζ = -18.9 mV) and a highly negative specific surface charge (q = -2.28 C/g) as a result of the dissociation of surface acidic functional groups of cotton cellulose (hydroxyl and carboxylic groups). On the other hand the treatment of cellulose fibres with cationic surfactants or quaternary ammonium...
ions leads to a significant modification of the fibre surface resulting in the reversal of charge. Cationised cotton, besides – COOH, has –NH₂ groups as well due to the bonded cationic compound, and it can be considered as Bronstead base, Equation 10.

In this paper a commercial product, long-chain cationic compound Sintegal V7, was applied in three different concentrations. Bonding of this long-chain cationic compound in cationisation causes a change in surface charge. In Figure 1b a model of the cationised surface is proposed together with the potential profile in the electrical interfacial layer. This adsorption, which is primarily electrostatic, reverses the original negative charge of the solid, occurring within the Stern layer at the inner Helmholtz plane. Because of long hydrophobic tails the next phase of adsorption results in tail-tail interaction, whereas the positively charged heads are directed from the solid toward the bulk of liquid. Such an excess of positive charge results in positive zeta potential as well. For that reason the zeta potential increases in cationisation with Sintegal V7 from ζ = -18.9 mV for P0 to ζ = -15.3 mV for P0.5, ζ = -14.9 mV for P1, and ζ = -13.7 mV for P2.

Besides the zeta potential at pH 10, it is important to know the isoelectric point (IEP) and point of zero charge (PZC). For determination of these points it was necessary to measure the change in zeta potential in dependence on the electrolyte pH and ionic surfactant addition. IEP is an important parameter in dyeing and finishing. Results obtained, presented in Table 2 and Figure 3, indicate that bleached cotton fabric has an IEP in the area of less than pH 2.5. In that pH area the number of ionic groups is higher than that on the fabric surface, therefore the correct value could not be determined. By cotton cationisation the IEP moves towards higher values depending on the concentration of the cationic compound applied (from 3.82 for P0.5 to 4.34 for P2).

The point of zero-charge (PZC) was determined at pH 10 because in that pH area the zeta potential has the highest and constant value. The results presented in Table 2 and in Figure 3 show that as the surface is more negative, it adsorbs more cationic surfactants to reach zero-charge. Therefore bleached cotton fabric has the highest PZC (67.72 µg/ml) and the most positive fabric, and that cationised with 2 g/l Sintegal V7 the lowest (P2 = 49.94 µg/ml), respectively.

The specific amount of surface charge determined by the back-titration method confirms assumptions about the cotton fabric surface charge placed by the zeta potential and PZC. Bleached cotton fabric has a highly negative surface charge. Cationisation with different concentrations of Sintegal V7 significantly reduces the electrical negative charge to q = 0.

From the results of zeta potential at pH 10 and the specific amount of charge on the surface, it is obvious that all cationized cotton fabrics are significantly positively charged. Therefore these fabrics are an excellent substrate for the adsorption of anionic dyestuffs and surfactants.

For that reason in this paper the cotton fabric adsorption ability of anionic reactive dyestuffs with different functional groups was researched, the results of which are collected in Table 3.

As can be seen from Table 3 electrolyte addition to the dye bath increases dye stuff adsorption, which was expected because electrolyte neutralise the cotton surface’s negative charge as well as the dyestuff’s negative charge. Making dyestuff absorption easier. However, the electrolyte in the dyeing bath has another role as well - it increases the dyestuff’s chemical potential, moving the equilibrium distribution towards the fibre. In the dyestuff adsorption mechanism, cationised cotton partially replaces the role of cationic surfactants, which was confirmed by the zeta potential results. For that reason the results of dyeing cationised cotton without electrolyte can be explained as a contribution of the cationic compound to the exhaustion efficiency from the dye bath.

Table 3. Color intensity (K/S) and its increment (I) of cationised cotton fabrics dyed with anionic reactive dyestuffs with and without electrolyte addition.

<table>
<thead>
<tr>
<th>Dyestuff</th>
<th>Fabric</th>
<th>No electrolyte</th>
<th>10 g/l NaCl</th>
<th>50 g/l NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K/S</td>
<td>I, %</td>
<td>K/S</td>
</tr>
<tr>
<td>Ostazin Red H-3B</td>
<td>P0</td>
<td>0.51</td>
<td>-</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>P0.5</td>
<td>0.78</td>
<td>53</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>P1</td>
<td>1.26</td>
<td>147</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>1.50</td>
<td>194</td>
<td>1.65</td>
</tr>
<tr>
<td>Remazol Red B</td>
<td>P0</td>
<td>0.30</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>P0.5</td>
<td>0.39</td>
<td>30</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>P1</td>
<td>0.48</td>
<td>60</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>0.51</td>
<td>70</td>
<td>0.75</td>
</tr>
</tbody>
</table>
The comparative data indicate that the increment in the color intensity (I) of cationised cotton fabrics dyed with anionic reactive monochlorotriazine dyestuff Ostazin Red H-3B without the addition of NaCl is significantly higher than for cotton fabrics dyed with NaCl addition. For cationised cotton fabrics dyed with anionic reactive vinylsulfone Remazol Red B dyestuff this is not the case. The K/S values of cationised cotton fabrics dyed without NaCl addition, depending on the cationic compound concentration, are equal or greater compared to the K/S values of unmodified bleached cotton fabrics dyed with the addition of 10 g/l NaCl, regardless of the type of dyestuff reactive group. However, unmodified cotton fabrics dyed with the addition of 50 g/l NaCl have lower K/S values than cationised cotton without electrolyte addition. Considering this, it should be pointed out that cationic treatment can achieve savings in electrolyte consumption in reactive dying with vinylsulfone dyestuff, or even exclude monochlorotriazine dyestuff. Electrolyte in the dyeing bath can be considered as a cooperative contribution to cationic treatment.

Conclusion

Treatment of cotton fabrics with a commercial cationic compound does not change the chemical composition, but it does significantly alter the fibre surface. The change in the cotton fibre surface charge is proportional to the concentration applied – the higher concentration, the greater the zeta potential and surface charge.

The cationic compound adsorbed on the fibre surface increases the amount of positive functional groups which can bond anionic reactive dyestuff by ionic interaction, as well as cooperative contributions to increase the color intensity of the modified cotton fabric compared with an unmodified one.

Colour intensity is higher at a lower concentration of NaCl because in this case most of the dyestuff is in an ionic form and the attractive force between the anionic dyestuff and adsorbed cationic compound comes to full expression. When a standard amount of NaCl is added to suppress the ionic dissociation of dyestuff, ionic attraction is weaker, and the increase in the intensity of colour is less.

References