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Streaming Potential – Characteristics of Dyed Cotton Fibres

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Abstract
This paper deals with the surface properties of dyed cotton fibres, which were analysed by measuring the streaming potential. Diversified values of the potential were obtained for samples of fabrics dyed with model direct dyes 1-10. Changes in the streaming potential in water solutions of the model dyes were also analysed in order to determine the impact of polar functional groups of the dyes on their anion character. For a broader view of the phenomenon discussed, the analysis of the surface properties of fibres was supplemented with a description of the relative dye content in the fibre, using the K/S ratio.

Key words: *streaming potential, dyes/pigments, cotton fibres, microstructure.*

Introduction

Streaming potential measurements are a useful method of describing the surface properties of fibres. The properties of textile products in the chemical treatment of a fibre, including its dyeing, are largely dependent on the electric charge on its surface. The values of streaming current or potential determined can provide information about the energy of the interaction between the fibre and adsorbent, such as a dye.

Practically all colloidally dissolved substances and solid particles in water carry electric charges. This leads to a concentration of oppositely charged ions, the so-called counter-ions, on the colloid surfaces. If these counter-ions are separated from, or sheared off, the dissociated macromolecule or particle, a streaming potential can be measured in mV.

There have been many attempts to describe a fibre surface from the point of view of its chemical treatment. Researchers Ribitsch, Grancarić, Pusić and Stana-Kleinschek [1 - 5] were interested in how the changes in streaming potential depend on the preliminary treatment of textile products, such as mercerising or bleaching. For example, the potential of raw cotton fibre ζ is –12 mV because the functional groups of the first fibre wall are covered by hydrophobic substances, Grancarić [3]. The streaming potential value changes significantly after bleaching and dyeing. Compared with raw fibres, treated fibres become more electronegative as a result of the diversified purity level of their surface following chemical treatment, Pusić [4]. In recent years, the streaming potential has also been examined using solutions of dyes and auxiliary agents in order to determine their interactions, Rybicki [6]. The method presented here is also a useful source of general information about the surface properties of polymer materials, El-Gholabzourić [7].

Because of the simplicity of application and great choice of products available, direct dyes are a popular dye class used to dye cellulose. Most direct dyes have azo structures, particularly in the disazo and trisazo chemical classes. Benzidine is one of the amines used. It is well known that benzidine and its derivatives, such as 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine and 3,3'-dichlorobenzidine, are both mutagenic amines and human carcinogens, Messerly & Freeman [8 - 9].

Benzidine derivatives containing propyl or butoxy substituents ortho to the amino groups are nonmutagenic, as are, in the standard Ames test, dyes based on these substituents, Freeman [9]. In this study, direct dyes were used in which 2,2'-dimethyl-5,5'-dipropoxybenzidine and 5,5'-dipropoxybenzidine were employed as potential alternatives to benzidine.

Experimental

For examination, ten model azo dyes were selected and synthesised at North Carolina State University, Raleigh, USA, Bae [10]. ***Figure 1*** (see page 96) shows the dyes selected for examination.

3% dyeing (owf) was carried out under neutral conditions at a 60:1 liquor ratio. A sample of cotton fabric was wetted with hot water and added to a dyebath. The bath temperature was raised to 95 °C and held there for 30 minutes. After adding 10% Na_2SO_4, dyeing was continued for 30 minutes. The dyed fabric was then rinsed with cold water and air-dried.

The K/S value calculated from the Kubelka-Munk equation and expressed by the remission ratio R was determined spectrophotometrically with the wavelength λ_{max}, Kuehni [11]. Samples of cut and dyed cotton fabrics weighing 0.2 g were selected for measurements in 30 cm^3 of distilled water. Streaming potential measurements were taken using a PCD 03 pH Particle Charge Detector manufactured by Mütek, Germany.

Results and discussion

A double electric layer is formed on the interfacial surface between the charged fibre surface and the water solution of electrolytes. The layer is a result of the dissociation of functional groups from the surface molecules of the fibres or the adsorption of ions from the solution surrounding the fibre. The streaming potential of natural fibres in distilled water is always negative. According to Jacobasch and Stackelberg [12 - 13], the potential ζ for cotton in water is –28.5 mV, while in KCl solution it is –35 mV. For wool in

Table 1. *Streaming potential and K/S values obtained for samples of cotton and wool dyed with model dyes 1-10.*

Dyes	Cotton		
	Streaming potential, mV	K/S	λ, nm
1	-890	3.097	540
2	-966	3.560	580
3	-973	0.211	580
4	-954	0.143	600
5	-1094	0.243	600
6	-943	0.096	600
7	-1056	0.011	560
8	-1023	1.194	580
9	-1047	5.058	580
10	-997	1.937	600

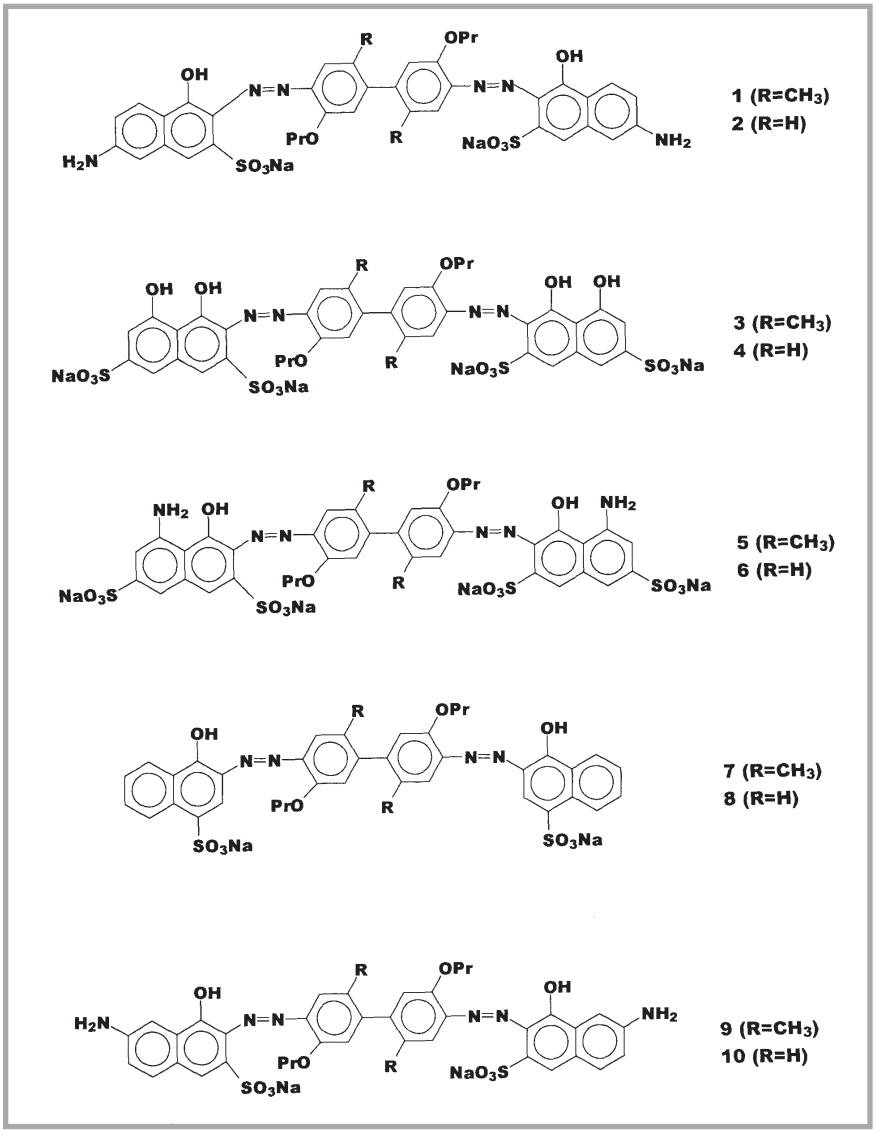

Figure 1. *Structures of model azo dyes.*

KCl solution, the value is –62 mV, Stackelberg [13]. A streaming potential can be successfully used for monitoring changes in the supermolecular structure of a fibre and its morphology, and the values obtained correlate with other physical and chemical examinations.

In this study, the streaming potential was measured for samples of cotton dyed with model direct dyes (***Table1***). For cotton fabrics, the potential was found to exceed –1000 mV for samples dyed with model dyes 5, 7 and 9.

Generally, the values of streaming potentials in water solutions obtained depend on the interaction between fibres and electrically charged molecules (e.g. surface-active substances and dyes), including the distribution of the charge both in the absorptive and diffuse parts of the double electric layer, Rybicki [14]. The impact of dyeing on the streaming potential properties of fibres has been analysed for a long time, Jacobasch [15]. The special role of the streaming potential is attributed to the sorption of dyes on the interfacial surface: the fibre–water solution of the dye. The structure of the double electric layer in the process of dyeing is complex because of the dyebath composition. Some dyes occur with inorganic salts, levelling agents and surface-active substances. The negative potential ζ of natural and synthetic fibres in a water solution with a direct dye is known to increase as the concentration of the dye in the dyebath grows, Suzawa [16], then it reaches a maximum and subsequently begins to decrease. These observations are attributed to the adsorption of dye anions on the fibre and the compression of the thickness of the double electric layer. The change in the surface adsorption of the dye is more than ten times greater for synthetic fibres than for natural fibres, Suzawa [16]. When direct dyes are used, surface adsorption of the dye is caused by the forming of hydrogen bonds and van der Waals forces between the dye and fibre.

Direct dyeing is a complicated and little understood process, although it seems very simple in terms of application. Hydrogen bonding between the hydroxy groups of cellulose and centres of electronegativity (nitrogen and oxygen atoms) in the dye molecule, especially those substituted with hydrogen atoms (as in =N–NH– and –OH), is widely acknowledged to contribute to the adsorption and retention of direct dye molecules. In this regard, it has been shown that intermolecular H-bonding is possible for each type of cellulosic hydroxy group on polymer chains in the amorphous regions of the fibre, Shore [17]. Almost all hydroxyl groups of cellulose in the fibre amorphous regions can create hydrogen bonds. The chemical structure of an individual dye determines the possibility of a breakup of fibre–fibre hydrogen bonds, with a simultaneous creation of fibre–dye bonds, Shore [17].

The ortho position of an –OH group (***Figure 1***) in relation to the azo bond suggests that hydrogen bonds may be created for all ten model azo dyes selected, Antonov, Szadowski [18 - 19]. For dyes with two strong electrodonor groups, $–NH_2$ and –OH, hydrogen bonds may be easily created.

The $–CH_3$ groups in dyes 1, 3, 5, 7, 9 cause additional steric hindrances and probably affect the scale of the destruction of the dyed fibres. Other centres of electronegativity in the dye molecule not participating in the creation of hydrogen bonds in the dye remain at the disposal of the cellulose -OH groups, Pielesz [20]. The possibility of the fibre-dye interactions suggested, combined with the structure of model azo dyes, as presented above, results in the highest values of the streaming potential for dyes 5, 7 and 9.

It is also interesting to observe the changes in the streaming potential value of water solutions of the model dyes (***Figures 2*** and ***3, Table 2***) in order to evaluate their ion character. The direct model dyes selected for examination make up a group of nongenotoxic azodyes of simi-

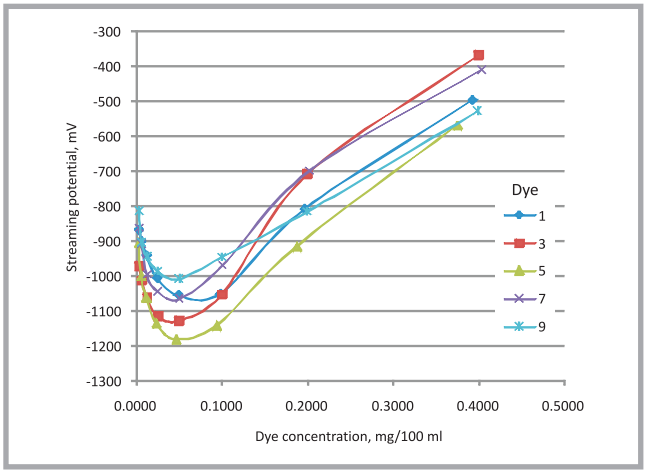

Figure 2. *Streaming potential diagram in a water solution of dyes 1, 3, 5, 7, 9.*

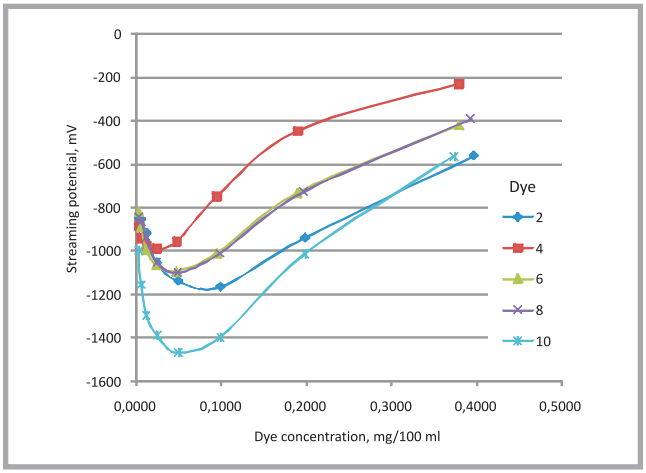

Figure 3. *Streaming potential diagram in water solution of dyes 2, 4, 6, 8, 10.*

lar structure but with different numbers of the –OH, $–NH_2$ and $–SO_3Na$ functional groups. Earlier, Lokhande [21]. The influence of the $–SO_3H$ group occurring in the molecule of the adsorbed dye was analysed to determine the streaming potential of the fibre.

Generally, all the direct dyes selected for this examination (***Table 2***) revealed a highly electronegative streaming potential, which proves their anion character, resulting from the presence of sulfonic groups in the molecule. For all the dyes analysed, this potential decreases considerably as the dye concentration in the dyebath grows; it is negative and varied depending on the ion character of the compounds.

Azo dyes, in general, are well known to form dimers or higher aggregates at high concentrations of the solution, Murakamei [22], because of the presence of dye-dye intermolecular interactions. Aggregation is induced by a high ratio of relative molecular mass to ionic group content, Shore [17]. The relative tendencies to aggregate depend on the different dye structures. For the model direct dyes analysed in this study (***Figure 1***), correlations with reference dyes 7 and 8 should be sought. The values of streaming potential in water solutions of dye obtained (***Table 2***) can be presented as the following inequalities (***Figure 2*** and ***3***):

dye 1, dye 9 > dye 7 > dye 3, dye 5
and
dye 2, dye 10 < dye 8 <dye 4, dye 6.

For example, under given conditions of temperature and electrolyte concentration, model direct dye 8 is much more highly aggregated than other dyes (***Figure 1***). Perhaps dye 8 aggregates more because it has fewer SO_3 groups, which are arranged in such a way that the planar central region of the molecule is subject to less steric bulk than in the other dyes. All of the dyes are of the disulphonated disazo type; however, it can be presumed that the two phenolic groups and the hydrogen in dye 8 provide much greater scope for intermolecular hydrogen bonding (***Figure 1***).

The dye exhaustion degree (E_k) was determined by colorimetry, Pielesz [23], with the dye concentration in the dyebath measured before and after dyeing. As the examination showed, cotton fibres dyed

Table 2. *Streaming potential in water solutions of dyes 1 - 10.*

Dye	mg of dye/100 ml	Streaming potential, mV	Dye	mg of dye/100 ml	Streaming potential, mV
1	0.0031 0.0061 0.0123 0.0246 0.0492 0.0983 0.1966 0.3932	-870 -902 -943 -1008 -1057 -1053 -810 -497	2	0.0031 0.0062 0.0124 0.0248 0.0496 0.0993 0.1985 0.3970	-852 -856 -919 -1055 -1138 -1166 -940 -562
3	0.0032 0.0063 0.0125 0.0250 0.0500 0.1000 0.2000 0.4000	-972 -1013 -1062 -1115 -1129 -1054 -708 -368	4	0.0030 0.0059 0.0119 0.0238 0.0475 0.0950 0.1899 0.3798	-885 -941 -978 -991 -958 -750 -447 -229
5	0.0030 0.0059 0.0117 0.0235 0.0469 0.0939 0.1877 0.3754	-906 -1001 -1063 -1137 -1182 -1143 -916 -569	6	0.0030 0.0059 0.0119 0.0238 0.0475 0.0950 0.1899 0.3798	-820 -887 -997 -1063 -1095 -1012 -734 -422
7	0.0032 0.0063 0.0127 0.0253 0.0506 0.1012 0.2024 0.4048	-864 -909 -998 -1046 -1067 -971 -700 -409	8	0.0031 0.0062 0.0123 0.0246 0.0493 0.0985 0.1970 0.3940	-846 -865 -934 -1052 -1101 -1012 -729 -392
9	0.0031 0.0062 0.0125 0.0249 0.0499 0.0997 0.1995 0.3990	-815 -906 -946 -988 -1010 -948 -817 -528	10	0.0031 0.0061 0.0124 0.0248 0.0497 0.0994 0.1987 0.3740	-1001 -1159 -1299 -1392 -1473 -1403 -1018 -566

with dyes 8 and 10 had the best sorption properties. But the lowest values of the streaming potential were observed for dye 10 (***Figure 2***). In principle, the results obtained correspond with the dye exhaustion curve. However, it should be stressed that the process of fibre dyeing is a complex phenomenon (the adsorption, absorption and diffusion of dyes into the fibre, the impact of electrolytes, the compression of the double electric layer), therefore it is groundless to draw quantitative conclusions.

The results described above confirm the tests conducted by Ehrler [24], who found out that the streaming potential is less dependent on the chemical structure of the fibre and its swelling than on the wetting of the fibre by solutions and the kind and concentration of levelling agents, because of the interaction between the fibre and auxiliary agents. Moreover, the streaming potential is dependent on the dye molecules adsorbed on the fibre surface but not on the total quantity of the dye absorbed by the fibre. Therefore, the K/S ratio is used to describe the dyeing process more extensively and, in particular, to determine the relative content of the dye in the fibre, Mielicki [25]. The light that falls on the surface of a coloured body, such as a textile product, is partly absorbed by it, then diffused, reflected and transmitted. A relation was introduced that combines the absorption coefficient K and diffusion coefficient with the reflection (remission) coefficient R of light falling on a body's surface, its thickness allowing for radiation transmission:

$$K/S = (1-R)^2 / 2R = kc_w$$

For textile products with the same structure, the K/S value calculated from the Kubelka-Munk equation and expressed by the remission coefficient R is proportional to the dye concentration in the fibre c_w.

The values of K/S obtained (***Table 1***) show that the highest dye concentration in cotton cellulose is expected for fabric dyed with dyes 1, 2 and 9. For dye 1, K/S is 3.097 (K = 540 nm); for dye 2, K/S is 3.56 (K = 580 nm), while for dye 9, it is 5.058 (K = 580 nm). The remaining dyes penetrate fibres with significantly smaller values of K/S.

Conclusions

It should be mentioned that the process of dyeing natural fibres, being a complex and multi-stage phenomenon, can only be described using a variety of experimental techniques. For natural polymers with a complex supermolecular structure, such as cotton cellulose and wool keratin, drawing conclusions must always be partly based on estimations.

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CORRECTION:

Please note that in issue No. 4 (75)/2009 of our journal, due to an oversight by the authors, the acknowledgements were omitted from the paper entitled *"Influence of Fibre Formation Conditions on the Properties of Nanocomposite PAN Fibres Containing Nanosilver"* by T. Mikołajczyk and G. Szparaga. They should have appeared as follows:

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