Scientific paper

Dyeing of Papermaking Fibers with Dyes of Various Structural Types as a Means for Fiber Surface Characterization

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Abstract

Birch kraft fibers of various composition with respect to lignin, hemicelluloses and cellulose and cotton were stained with cationic dyes belonging to different structural classes: Methylene Blue (MB), Crystal Violet (CV), 4-phenylazo-*N,N,N*-trimethylanilinium nitrate (TMY), Astra Blue (AB) and Alcian Blue pyridine variant (ABP). Adsorption isotherms measured at pH 8 were found to be in good agreement with Langmuir model. Methylene Blue and Crystal Violet exhibit adsorption proportional to the amount of anionic groups on fibers. A binding of a related cationic dye, 4-phenylazo-*N,N,N*-trimethylanilinium nitrate, is much lower. The behavior of cationic phthalocyanine dyes is more complex; besides their dependence on the quantity of anionic groups, these dyes exhibit marked affinity to fibers with low content of lignin. For phthalocyanines a different binding mechanism is apparent.

Keywords: wood fibers, cationic dyes, phthalocyanine dyes, carboxylic groups, lignin, hemicelluloses

1. Introduction

The fiber surface properties are the principal factor in the interfiber bonding – papersheet formation and they strongly influence the quality of paper products. Numerous functional groups are present on wood fiber surface as natural constituents or formed during the process of delignification and bleaching. Ionizable groups, e.g. carboxylic, sulfonic and phenolic give rise to negative charge on fiber surface and can be found on lignin, hemicelluloses and cellulose.[1] Besides, there is abundance of carbohydrate hydroxyl groups arising from hemicelluloses and cellulose in the fibers. All these functional groups are responsible for bonding of fibers to one another as well as of papermaking additives, dyes and other compounds to fibers. The knowledge of various types of dyes abilities of binding to individual constituents of papermaking fibers and/or functional groups present on the surface of these fibers is of great importance in designing printing inks suitable for printing on different types of papers and vice versa.

Methods of characterization of these groups are in constant development. A great deal of research in the last few years has been focused on the determination of anionic (carboxylate, sulfonate and phenolate) groups on fibers. Several analytical techniques (conductometric and potentiometric titration, polyelectrolyte adsorption, spectroscopic methods etc.)[2–4] are being applied and new ones introduced and tested, e.g. adsorption of Methylene Blue.

The use of MB for the determination of anionic sites on textile fibers began in the middle of the twentieth century with the work of Davidson.[5] He established that the binding of the dye is proportional to the content of carboxylic groups on cotton fibers although the binding of dye to hydroxyl groups is also possible. However the affinity in this case is lower (the term affinity in this paper is not used in a strict physical meaning but in a rather loose sense; the term recommend by some authors is substantivity). The adsorption of MB was found to be proportional to the amount of anionic groups on most types of papermaking fibers as well. Several methods for determination of the anionic groups were compared and the best correlation was established for dye sorption and conductometric titration.[3, 6, 7]

For the quantitative evaluation of lignin content on the surface of a single fiber the adsorption of Acridine Orange was investigated.[8] Yu et al.[9] studied the adsorption of two structurally different dyes on pulps varying in pore structure. The adsorption of various dyes on wood fibers was investigated by Drnovšek and Perdih[10–12] with the aim of discovering how the staining of fibers with structurally different dyes depends on fiber surface composition, and whether the staining can be applied for its determination. In these studies a large number of dyes of different structural types and ionic properties were investigated. Dyes were grouped according to their ability of binding to a fiber component which prevails on its surface. A certain degree of selectivity in the affinity of different groups of dyes to individual fiber constituents was established. The results demonstrate that cationic dyes exhibit a marked affinity to lignin, and cationic phthalocyanine dyes to hemicellulose part, while anionic direct dyes were found to be selective for the cellulose part of the fibers.

An important feature of dye molecules, which should be taken into account in adsorption studies, is their self aggregation. It can be observed by numerous physical and optical properties of the dyes; the most frequently used method is the UV-VIS spectrometry. In the spectra of dyes two absorption peaks usually appear; one corresponding to the monomer (at higher wavelength) and the other to di- and higher oligomers (at lower wavelength). The aggregation of MB was studied by several workers[13–16] and found that the association constant of the dimer in water is approx. 3×10^3 L mol^{-1}. Similar was found for CV,[17, 18] however with somewhat weaker association ($K_{\mathrm{ass}} = 7 \times 10^2$ L mol^{-1}). Aggregation of phthalocyanines was studied mainly on anionic species, but the behavior of the cationic analogues of equal charge is expected to be similar.[19–21] The association constants are in the range of 10^6 L mol^{-1}, which is considerably higher than that of MB. Aggregation of phthalocyanine dyes thus occurs at lower concentrations than that of MB and CV. With all types of dyes, with increasing concentration, higher oligomers also appear. Nevertheless the question appears, whether in the course of the adsorption process only monomer molecules adsorb, or does the adsorption of di- and higher oligomers take place as well. Numerous studies of adsorption of various dyes on clays, polyelectrolytes and other materials reveal that aggregation also occurs with the adsorbed dyes, the degree of which depends on the type of dye and the nature of adsorbent surface.[14, 22–25]

To resume the work of Drnovšek,[10–12] a more detailed study of the adsorption of dyes was undertaken. Three types of wood fibers differing from each other with respect to the proportion of lignin, hemicelluloses and cellulose, together with cotton were treated with two groups of cationic dyes. The first one comprises dyes with delocalized positive charge, such as MB and CV which are expected to exhibit pronounced affinity to lignin. The second group is represented by two phthalocyanine dyes with somewhat larger molecules and localized cationic charge on side-arms, Astra Blue (AB) and Alcian Blue pyridine variant (ABP), and expected affinity to hemicelluloses.

The selectivity found in previous studies had to be reinvestigated with the purpose of determining whether it is explicit enough to allow the general use of the measurement of dye adsorption for the determination of fiber composition. Selective binding of certain types of dyes on individual constituents of papermaking fibers can also be potentially applicable for rapid determination of fiber composition during the technological processes in papermaking and/or fiber production.

2. Experimental

2. 1. Materials

The experiments were carried out on four different kinds of fibers used as model substrates. Unbleached birch kraft (UBK Birch) pulp containing lignin, hemicelluloses and cellulose with Kappa number 21.8 (corresponding to approx. 3.6% of lignin[26]) was obtained under conventional kraft procedure. Industrial bleached birch kraft (BK Birch) pulp containing mostly hemicelluloses and cellulose, but little lignin (typical value for this type of fibers is approx. 0.1%), was used as purchased. Alpha-cellulose (α-BK Birch) was used as model substrate containing cellulose with lower content of hemicelluloses and lignin. The sample was prepared according to the standard procedure (TAPPI standard 203 om-93) from industrial bleached birch kraft pulp. As the cotton pulp sample the commercially available peroxide bleached cotton combers were used.

Before further analyses the pulps were soaked in water for a few hours and afterwards extensively washed with warm distilled water to remove all dissolved and colloidal substances, then filtered (the conductivity of filtrate was below 2 μS cm^{-1}) and stored in a refrigerator.

The following dyes belonging to different groups of dyes were used for the study of sorption. Caution! Some of the dyes (particularly Crystal Violet) present hazard to user and environment. Safety precautions should be observed.

Cationic dyes: Methylene Blue (C.I. 52015, Basic Blue 9) was recrystallized from ethanol. Crystal Violet (C.I. 42555, Basic Violet 3) was recrystallized from ethanol/ether solution.

4-phenylazo-*N,N,N*-trimethylanilinium nitrate (not a commercial dye, in this paper it will be named Trimethyl Yellow, TMY) was synthesized as follows: **4-phenylazo-*N,N,N*-trimethylanilinium iodide**.[27] A mixture of 2.25 g

(10 mmol) of 4-dimethylaminoazobenzene, 4 ml (20 mmol) iodomethane and 100 mL acetonitrile was stirred for 6 days at r.t. The brown precipitate, 4-phenylazo-*N,N,N*-trimethylanilinium iodide was filtered with suction, washed with cold water and dried. It was used directly in the preparation of 4-phenylazo-*N,N,N*-trimethylanilinium nitrate.

4-phenylazo-*N,N,N*-trimethylanilinium nitrate (TMY). 4-phenylazo-*N,N,N*-trimethylanilinium iodide (2.06 g, 5.6 mmol) was dissolved in 100 ml of warm ethanol and the solution of silver nitrate (0.95 g, 5.6 mmol) in 100 ml ethanol was carefully added. Precipitated silver iodide was filtered off. Filtrate was concentrated under reduced pressure and diluted with *tert*-butyl methyl ether. 1.41 g (83%) of 4-phenylazo-*N,N,N*-trimethylanilinium nitrate was obtained as orange crystals, mp 235-237 °C. UV: λ_{max} = 314 nm, (ε = 16 100 L mol^{-1} cm^{-1}); 420 nm (ε = 2380 L mol^{-1} cm^{-1}). ^{1}H NMR (DMSO-d_6) δ/ppm: 3.70 (s, 9H), 7.65 (m, 3H), 7.96 (m, 2H), 8.09 (d, *J* = 9.3 Hz, 2H), 8.23 (d, *J* = 9.3 Hz, 2H). Elemental analysis: calcd. for $C_{15}H_{18}N_4O_3$: C 59.59, H 6.00, N 18.53; found: C 59.47, H 6.04, N 18.35. This dye was prepared as a nitrate salt because the corresponding iodide is virtually insoluble in water.

All attempts to recrystallize phtalocyanine dyes Astra Blue (Basic Blue 140) and Alcian Blue pyridine variant (C.I. 74240) were unsuccessful and they were used as purchased.

The purity of recrystallized dyes was confirmed with ^{1}H NMR and UV-VIS spectroscopy and elemental analyses. All other chemicals used were of analytical grade and were used as purchased.

2. 2. Methods

Carboxylic acid group content in pulp was determined by standard conductometric titration method (SCAN standard CM 65:02). A glass pH electrode was also immersed in the titration vessel. Hexeneuronic acid groups (HexA) were analyzed by a selective hydrolysis with mercuric acetate and UV-VIS spectrophotometry.[28] Uronic acids were determined by acid methanolysis followed by GC.[29]

Equilibrium sorption studies, typical procedure. Wet sample of fibers (containing 100 mg of oven dried fibers) was weighed, transferred into the Erlenmeyer flask and soaked in 30 mL of distilled water. After few minutes, 7 mL of 0.025 M $Na_2B_4O_7$/HCl buffer solution (pH 8.0), an appropriate volume of distilled water and dye stock solution (1 mmol L^{-1}) was added in order to achieve the appropriate initial dye concentration. After 30 min the mixture was filtered and the first 10–20 mL of the filtrate discarded. Dye concentration was measured on a CARY 50 model UV-VIS spectrophotometer at λ_{max} of each dye.

Influence of pH on sorption. Adsorption at four pH values: 6.5, 8.0, 8.5 and 9.0 at dye concentration of 0.025 mmol L^{-1} was measured by the above procedure. The $Na_2B_4O_7$/HCl buffer solution (c = 0.02 M) was applied in all cases, except for pH = 6.5, where KH_2PO_4/NaOH was used.

3. Results and Discussion

The amounts of ionizable carboxylic (and/or phenolic) groups on fibers were determined by conductometric titration (Fig. 1, Table 1).

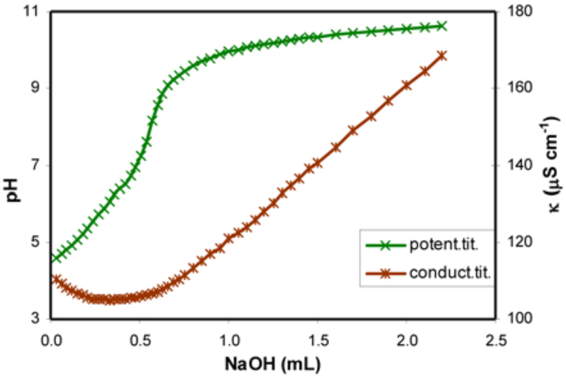

Figure 1. Conductometric and potentiometric titration curves for the titration of bleached birch kraft pulp with NaOH.

During the conductometric titration of fibers with NaOH, also the pH of the suspension was monitored. In the beginning, a gradual increase of pH with the amount of added NaOH is observed. At pH > 7 the curve becomes steeper, indicating the complete ionization of carboxylic groups. The equivalent points of conductometric and potentiometric titrations coincide fairly well.

Carboxylic groups in fibers belong to different types of carboxylic acids, e.g uronic and hexeneuronic acids

Table 1. Amount of carboxylic groups and uronic acids in birch kraft pulps

Sample	COOH groups[a] µmol g^{-1}	HexA[b] µmol g^{-1}	Uronic acids[c] µmol g^{-1}
UBK Birch[d]	147	40.6	18.5
BK Birch[e]	55.4	0.85	5.7
α-BK Birch[f]	34.4	0.29	5.5
Cotton[g]	12.9	–	–

[a] Determined by conductometric titration. [b] Hexeneuronic acids (HexA) determined spectrophotometrically by selective hydrolysis with $Hg(OAc)_2$. [c] Determined by acid methanolysis and GC. [d] Laboratory prepared unbleached birch kraft pulp. [e] Industrial bleached birch kraft pulp. [f] α-cellulose, prepared from BK Birch by hydrolysis with NaOH. [g] Cotton combers, peroxide bleached. Uronic acids not determined.

from polysaccharides as well as to those originating from the oxidation of lignin. In order to characterize fibers as much as possible, hexeneuronic and uronic acids were also determined.

According to conductometric and potentiometric titrations, the majority of carboxylic groups ionize between pH 3 and 7–8. It was expected that the amount of dye which gets adsorbed, depends on the degree of ionization of acid groups on fibers, therefore the adsorption of dyes was studied in the pH range where ionization is anticipated to be nearly complete (Fig. 2). On the basis of this study we decided to make further measurements of the adsorption at pH = 8, where the adsorption of most dyes is at maximum or at least leveled (the actual pH values in buffered working suspensions were in the range 7.7–7.9).

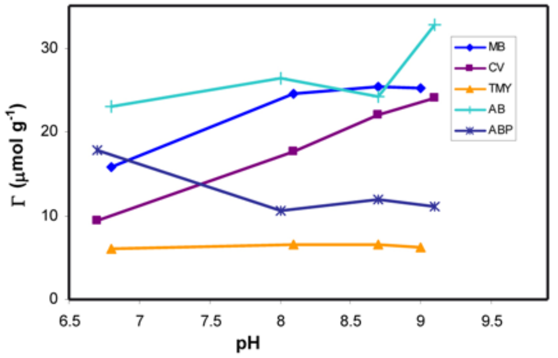

Figure 2. Amount of adsorbed dyes on bleached birch kraft pulp as a function of pH (Note that these measurements were not made at the saturation concentration of the dye).

The adsorption capacity of fibers was evaluated by the amount of the adsorbed dye (at 20 °C):

$$\Gamma = ([D]_0 - [D]) \times V/m \qquad (1)$$

where Γ is the equilibrium concentration of dye adsorbed (μmol g^{-1}), $[D]_0$ and $[D]$ are the initial and the equilibrium concentrations of dye in solution, respectively, m is the mass of fibers and V is the volume of solution.

The adsorption was studied in a broad range of concentrations of dye and the results fit best the Langmuir model (Eq 2, Fig. 3 and 4, fit to Freundlich model is worse), in accordance with numerous earlier studies:[5, 6, 30–33]

$$\frac{[D]}{\Gamma} = \frac{1}{\Gamma_{\max} \cdot K_L} + \frac{[D]}{\Gamma_{\max}} \qquad (2)$$

where Γ_{max} is maximum sorption capacity corresponding to monolayer coverage (μmol g^{-1}) and K_L is a Langmuir constant (L mol^{-1}).

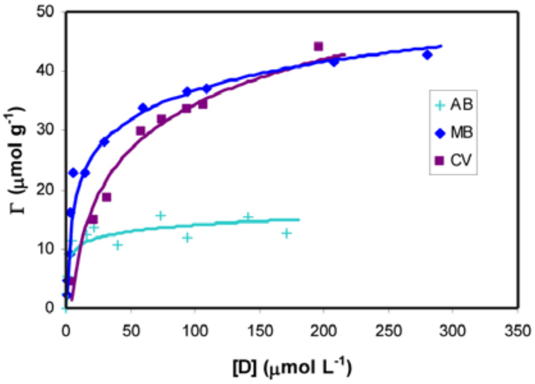

Figure 3. The adsorption isotherms of Astra Blue, Methylene Blue and Crystal Violet on bleached birch kraft pulp at pH = 8.

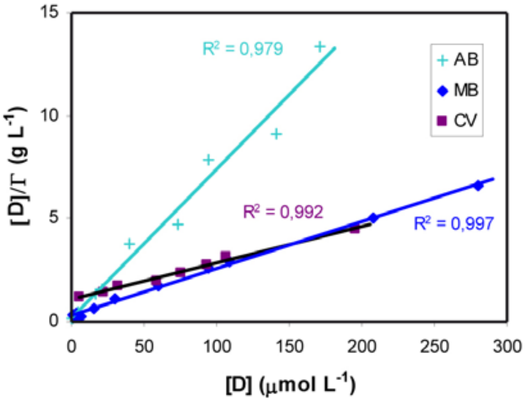

Figure 4. Langmuir plot of the adsorption of Astra Blue, Methylene Blue and Crystal Violet on bleached birch kraft pulp at pH = 8.

Fibers contain acidic ionizable groups, mostly carboxylic (small amount of acidic phenolic groups (p*K*a 7–8) may also be present) which ionize extensively at higher pH values (Fig. 1).[1] The adsorption of dyes on papermaking fibers is expected to be pH dependent, since the dyes applied are cationic and attractive interactions between dye cations and anionic sites on fibers are operating.[3, 5] First we tried to find a pH, suitable for adsorption studies for all structurally different dyes, which we intended to apply. One would expect for cationic molecules the adsorbed amount to be proportional to the negative charge on fibers, i.e. the increase with pH until the complete ionization of acidic groups (pH 7–8). In Fig. 2, very different pH-adsorption profiles of dyes can be observed. MB exhibits almost the expected increase with pH until a plateau is reached at pH ~8. For CV, the adsorption increases steadily and no plateau is observed. The curious behavior of Astra Blue (AB), which exhibits a repeated increase above pH 8.5, can be rationalized by the precipitation of the dye at higher pH values. Phthalocyanine dye AB (Fig. 5) is a tertiary amine and its ionic charge begins

Table 2. Amount of dyes adsorbed on fiber samples[a]

Sample	UBK Birch		BK Birch		α-BK Birch		Cotton	
	Γ_{max} μmol g^{-1}	K_L L mol^{-1}	Γ_{max} μmol g^{-1}	K_L L mol^{-1}	Γ_{max} μmol g^{-1}	K_L L mol^{-1}	Γ_{max} μmol g^{-1}	K_L L mol^{-1}
MB	147	0.049	44.1	0.074	23.0	0.084	9.4	0.029
CV	152	0.042	57.1	0.016	24.3	0.024	–	–
AB	50.5	0.068	13.7	0.68	13.0	0.23	17.4	5.0
ABP	43.4	0.072	11.5	0.27	16.5	0.13	–	–
TMY[b]	12.5	0.03	3.6	–	1.5	–	–	–

[a] Maximum adsorbed amount (Γ_{max}) of the dye according to Langmuir model at pH = 8.

[b] The scattering of the data-points was substantial due to low adsorbed amounts of TMY. The values of K_L are not very reliable and only a few are reported.

to decline above that pH, leading to the lowering of the solubility of the compound in water. The precipitation was indeed experimentally observed. Structurally similar Alcian Blue pyridine variant (ABP, Fig. 5) bearing constant cationic charge, exhibits first a decrease with plateau at pH ~8 and no precipitation. The adsorption of TMY is virtually pH independent. The pH-sorption profiles for MB on three types of fibers (unbleached and bleached birch kraft pulps and α-cellulose) are substantially similar, except for the amount of adsorbed dye.

Characterization of fibers by sorption studies is based on the amount of a dye adsorbed per unit mass of fibers. The adsorption isotherms of the dyes were measured to find the optimal dye concentration with which to do the staining. Our aim was to find a dye concentration that would fully saturate the binding sites on the fiber and would allow the use of a single point value as a measure of the adsorption capacity. A complete isotherm was first determined for each dye on each type of fibers. From measured isotherms, Langmuir constants K_L were derived as the intercept on *y*-axis from the Eq 2. The Langmuir constant is a measure of affinity of the adsorbate to adsorbent and could be potentially applicable to the assessment of the interactions between dye and fiber surfaces. Unfortu-

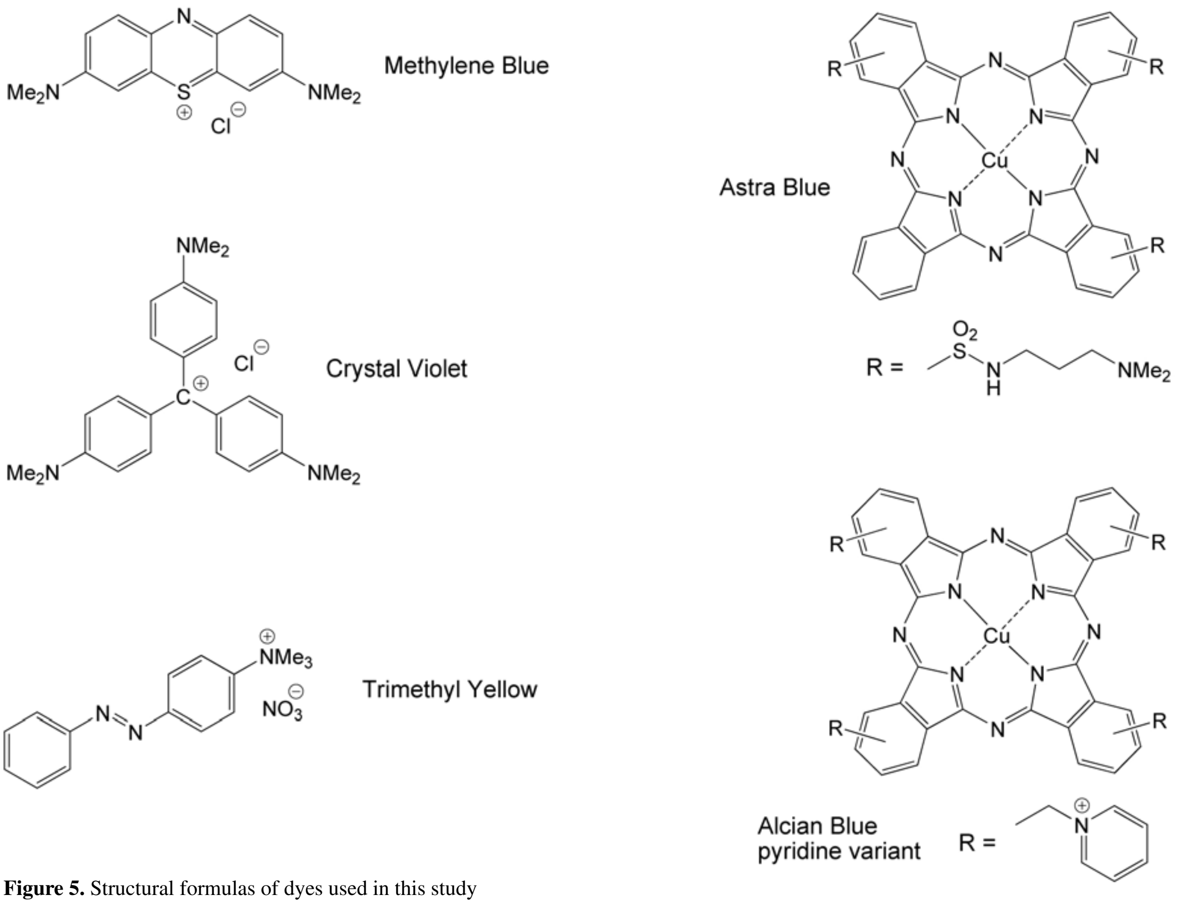

Figure 5. Structural formulas of dyes used in this study

nately, the measuring uncertainty in determining intercept on *y*-axis is considerable and the values obtained are very approximate. Nevertheless, it can be noticed (Table 2), that K_L for CV and MB are fairly independent on the fiber composition, being 0.02–0.04 and 0.05–0.08 L mol^{-1} for CV and MB, respectively. On the other hand, AB and ABP exhibit higher affinity difference between unbleached and bleached BK fibers, indicating lower affinity of these dyes to lignin rich fibers.[11]

Another parameter obtained from Langmuir isotherm is maximum sorption capacity (Γ_{max}), which corresponds to the amount of the dye adsorbed under the conditions of saturation. From data in Table 2 and Fig. 6 a good correlation of the amount of adsorbed MB and also CV vs. the amount of COOH groups determined by conductometric titration can be noticed. MB was extensively studied as an indicator of the amount of anionic (e.g. carboxylate) groups on fibers. These results show that the adsorption of CV is similar and also this dye (and probably some others) could serve the same purpose. It is interesting, that the two dyes exhibit similar behavior despite not very alike structures. MB has a flat, oblong molecule with dimensions 16 × 7 Å,[34, 35] while CV is a triangular, propeller-shaped molecule with a base of 16 Å.

Most of the negative charge on fiber surface can be attributed to carboxylate groups. The electrical charge in carboxylate is delocalized predominantly over three atoms, thus forming a rather small cloud of the negative charge (relatively hard Lewis base). The fairly good agreement of adsorbed amount of cationic dyes with the negative charge on fiber surface led us to the idea that the binding of the dye molecules, bearing comparatively small clouds of positive charge (relatively hard Lewis acids) might be even stronger than that of the common cationic dyes with strongly delocalized positive charge (soft Lewis acids, e.g. MB and CV). A cationic dye with more localized positive charge, namely 4-phenylazo-*N,N,N*-trimethylanilinium nitrate (named here as Trimethyl Yellow, TMY) was tested and the results of the adsorption measurements disproved our expectations.[36] The Γ_{max} value of TMY is more than 10-fold lower than those of MB and CV, although it exhibits the same trend of dependence on the amount of carboxylate. It seems that the binding of the cationic dyes to the negatively charged carboxylate groups on fibers is stronger when the positive charge of the cation is delocalized over broader area. Moreover, the binding of this dye is virtually independent on pH. The adsorption of a cationic compound with a related structure, a quaternary ammonium derivative of benzotriazole (i.e. both compounds are aromatic with localized cationic charge) was reported to be nearly proportional to the anionic charge on fibers.[31] At this stage, it is difficult to draw any conclusions about the mechanism of binding of this type of compounds to fibers.

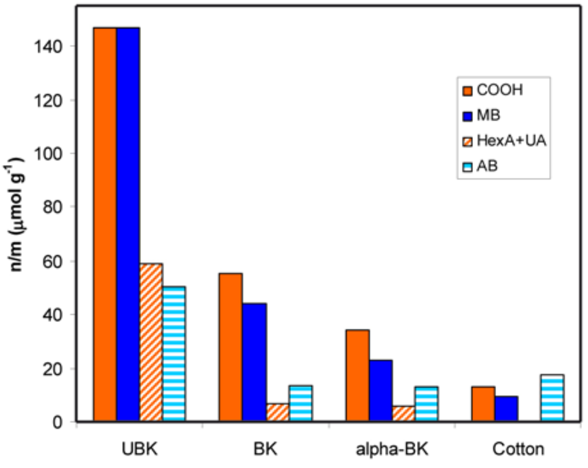

Figure 6. Correlation of the Γ_{max} and the amount of acid groups on fibers. COOH total amount of carboxylic groups, HexA + UA sum of uronic acids.

Molecules of two phthalocyanine dyes are likewise cationic with the electrical charge 3+ and 4+ for AB and ABP, respectively. The central parts of molecules are planar (base of the planar phthalocyanine moiety is ~15 Å) with flexible side-chains bearing the positive charge. The Γ_{max} for AB and ABP is lower than for MB and CV with all three types of birch fibers. Considering the model that one negative charge on fiber binds one positive charge on the dye molecule, than the Γ_{max} for the two phthalocyanine dyes of 1/3 (for AB) and 1/4 (for ABP) of that for MB could be expected. Indeed, when the values of Γ_{max} for AB and ABP in Table 2 are multiplied by 3 and 4, respectively, figures which roughly match the corresponding values for MB and CV are obtained for UBK and BK fibers. Interestingly, in fibers with lower content of hemicelluloses and lignin (α-BK and cotton) the binding of phthalocyanine dyes becomes independent on the amount of carboxylate groups and higher than predicted by the above model. One of the possible explanations could be the binding of phthalocyanine molecules to such regions of fibers, where polysaccharide chains are not packed tightly

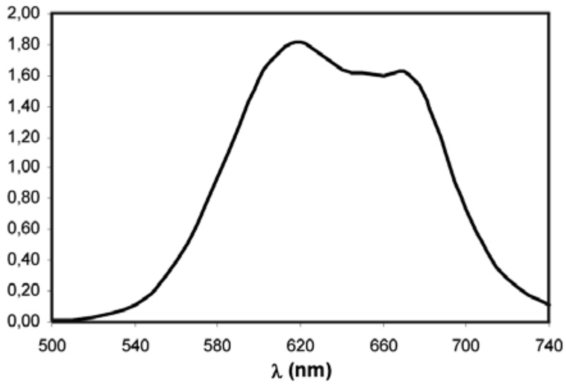

Figure 7. Reflectance (Kubelka-Munk units) spectrum of kraft fibers, stained with Astra Blue.[11]

but rather in loose, swollen structures. Large, planar molecules could penetrate into the gaps between cellulose or hemicelluloses chains, thus enhancing the binding beyond that governed by the negative charge on fibers.

Absorption spectra of all dyes applied in our study display two distinct absorption peaks, due to monomer and dimer or higher aggregates present in solution. The reflectance spectra of stained fibers exhibit similar patterns, indicating that the adsorbed dyes aggregate as well, or the aggregates adsorb. In Fig. 7 the reflectance spectrum of fibers dyed with AB is shown, however the spectra of fibers stained with MB and CV are related. Since the adsorption fits well to the Langmuir model, it seems reasonable, that the following equilibria are operating:[37]

$$[\text{monomer}_{(\text{sol})} \rightleftarrows \text{dimer}_{(\text{sol})}] + \text{fibers} \rightleftarrows [\text{monomer}_{(\text{ads})}, \text{dimer}_{(\text{ads})}]. \qquad (3)$$

High values of association constants for charged phthalocyanines indicate relatively strong intermolecular forces operating between their molecules, despite higher electrical charge compared with MB or CV. These forces are of various origin, however in water a significant part can be attributed to hydrophobic interactions since these molecules contain large uncharged central parts. Hydrophobic interactions can operate between dye molecules themselves, as well as between dyes and amphiphillic carbohydrate chains. They can be rather strong when dye molecules intercalate between carbohydrate chains, thus excluding water from the channels. Such interactions are particularly well known in protein-carbohydrate systems, where aromatic amino acid residues are engaged.[38, 39]

4. Conclusions

The adsorption of cationic dyes is influenced by the amount of negative charge on fibers, although other factors are also important. Some dyes, particularly those with strongly delocalized electrical charge, such as MB and CV obey this rule rather strictly. The adsorption of MB was shown previously to be of use as a measure of the amount of anionic groups on cotton or papermaking fibers, but obviously there are also some other dyes with similar adsorption characteristics. On the other hand, the cationic charge solely is not a sufficient condition to bring about strong adsorption to the negatively charged fibers; the charge distribution and/or the shape of the molecule also play an important role. Cationic phthalocyanine dyes also exhibit dependence on the amount of carboxylate groups to some extent, however on fibers with low content of carboxylate, the adsorption tends to increase, and apparently different binding mechanisms prevail. A certain degree of specificity to fibers low in lignin is apparent.

The idea of selective staining using different structural and ionic kinds of dyes with the purpose of determining the contents of individual constituents of papermaking fibers nevertheless seems to remain an achievable goal. As the binding of particular types of dyes is a complex function of the chemical composition, as well as of the morphological properties of fibers, the method might be applicable to individual types of fibers with respect to their origin and preparation.

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Povzetek

Sulfatna vlakna breze z različnim razmerjem med ligninom, hemicelulozami in celulozo ter vlakna bombaža smo barvali s kationskimi barvili različnih strukturnih tipov: metilensko modro (MB), kristalno vijolično (CV), 4-fenilazo-*N*,*N*,*N*,-trimetilanilinijev nitrat (TMY), astra modro (AB) in alcian modro – piridinska varianta (ABP). Adsorpcijske izoterme, merjene pri pH = 8 se dobro ujemajo z Langmuirovim modelom. Metilensko modro in kristalno vijolično se adsorbirata sorazmerno z množino karboksilnih skupin na vlaknih, vezava sorodnega barvila, 4-fenilazo-*N*,*N*,*N*,-trimetilanilinijevega nitrata pa je bistveno manjša. Obnašanje kationskih ftalocianinskih barvil je bolj kompleksno. Njuna adsorpcija je do neke mere odvisna od vsebnosti karboksilnih skupin, po drugi strani pa izkazujeta znatno afiniteto do vlaken z nizko vsebnostjo lignina, kar kaže na to, da je način vezave teh barvil drugačen.