Interaction of Maleic Acid Copolymers with Methylene Blue in the Presence and Absence of Melana Fibers

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In this paper are presented structural parameters that influenced the metachromatic phenomenon induced by two maleic acid copolymers in form of sodium salts, as anionic partners. One is hydrophilic, namely the copolymer sodium maleate-vinyl acetate, (NaM-VA), and the other is a hydrophobic one, namely sodium maleate-styrene copolymer (NaM-S). The cationic dye was Methylene Blue. The correlations between UV-Vis spectrum data and those of spectral remission are also discussed.

Keywords: maleic acid copolymers, Methylene Blue, metachromasy, Melana fiber, spectral remission, K/S values

Metachromasy represents the color change of a dye when it interacts with a polyelectrolyte in aqueous solution, which is reflected in changes in the absorption spectrum of the dye. Ehrlich has observed first this phenomenon and noticed changes in color when animal or vegetable tissues are in contact with a dye [1].

Metachromasy was also observed in the case of interactions between dyes and polyelectrolytes too, and many studies have been carried out concerning the effects of the interaction on absorption and fluorescence properties, the type of dyes that interacting with polyelectrolytes, lead to metachromatic shift, and the type of polyelectrolytes that can serve as substratum for metachromatic dyes. The polyelectrolytes that induce metachromatic color shift are called chromotropes. The effect has been observed between positively charged dyes and polyanions or between negatively charged dyes and polycations. The color change can be dramatic or subtile, and can be quantified by spectral changes in the UV-visible region of the spectrum. Various types of metachromasy, however, have been observed for different combinations of dyes and polyelectrolytes [2-6].

In the previous study was presented the influence of the chemical structure of the partners involved in metachromatic interactions: two dyes, CV or VBB, as well as of the polyelectrolytes NaM-VA or NaM-S [7]. In this study are discussed chemical behaviour and structural aspects of partners and complexes metachromatic of NaM-VA/MB or NaM-S/MB systems in the presence and absence Melana fibers.

Experimental part

Material and methods

Dye: Merck reactive MB, used without purification or other modifications. The dye chemical structure is presented in the figure 1.

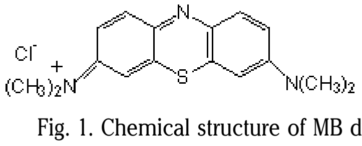


Fig. 1. Chemical structure of MB dye

Polyelectrolytes: a copolymer of the maleic acid with vinyl acetate (NaM-VA) and a copolymer of the maleic acid with styrene (NaM-S), both in the form of natrium salt. They were obtained from copolymer of the maleic anhydride with vinyl acetate or styrene synthesised in laboratory using methods of our own or from literature [8-9]. The polyelectrolytes are illustrated in figure 2.

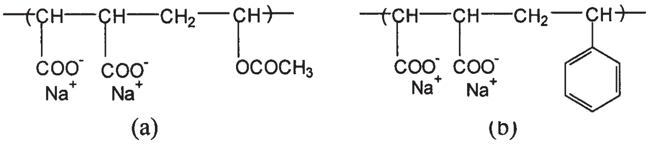
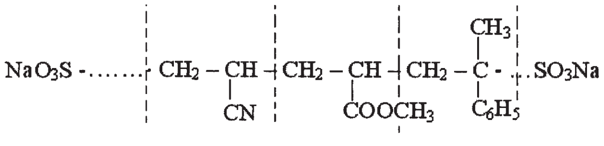


Fig. 2. Chemical structures of copolymers: natrium maleate with vinyl acetate (NaM-VA) (a) and natrium maleate with styrene (NaM-S) (b)

Melana Fibre: The Melana Fibre is a polyacrylonitrile fibre based on a ternary polymer (acrylonitrile, vinyl acetate, α-methylstyrene) obtained through a radical polymerization reaction initiated in the redox system with potassium persulphate - natrium metabisulphite, its schematic structure being presented in figure 3 [4, 10-13].



$$NaO_3S\text{-}\cdots\cdots CH_2-\underset{CN}{CH}-CH_2-\underset{COOCH_3}{CH}-CH_2-\overset{CH_3}{\underset{C_6H_5}{C}}\text{-}\cdots SO_3Na$$

Fig. 3. Schematic structure of Melana fiber

The method. One records the UV-Vis spectra for the NaM-VA/MB and NaM-S/MB, system, at ratios [P]/[D] from 0 up to 1.3, where [P] is the concentration of the polyelectrolyte, and [D] the concentration of dye. In all experiments, the concentration of dye is maintained as constant (2 . 10^{-6} eq/L), while the polyelectrolyte concentration is varied (0.2 . 10^{-6} ÷ 2.6 . 10^{-6} eq/L). The UV-Vis spectra were recorded on a Specord Carl Zeiss Jena M42 apparatus [4-6].

Dyeing procedure. Series of 6 dyeing operations of 1g for each coloristic position of Melana fibres were performed

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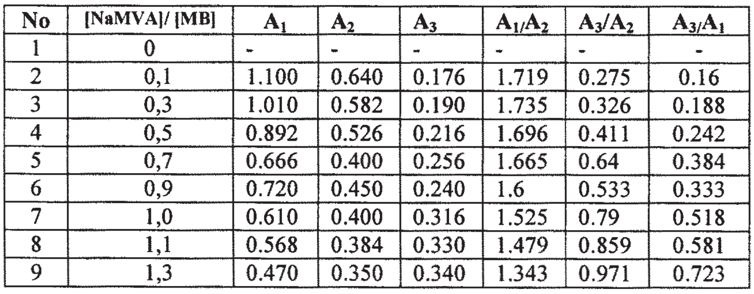
Table 1
VALUES OF THE A_3/A_1, A_3/A_2 AND A_1/A_2 RATIOS FOR THE NaM-VA/MB IN TERMS OF THE NEUTRALIZATION FACTOR α



No	[NaMVA]/ [MB]	A_1	A_2	A_3	A_1/A_2	A_3/A_2	A_3/A_1
1	0	-	-	-	-	-	-
2	0,1	1.100	0.640	0.176	1.719	0.275	0.16
3	0,3	1.010	0.582	0.190	1.735	0.326	0.188
4	0,5	0.892	0.526	0.216	1.696	0.411	0.242
5	0,7	0.666	0.400	0.256	1.665	0.64	0.384
6	0,9	0.720	0.450	0.240	1.6	0.533	0.333
7	1,0	0.610	0.400	0.316	1.525	0.79	0.518
8	1,1	0.568	0.384	0.330	1.479	0.859	0.581
9	1,3	0.470	0.350	0.340	1.343	0.971	0.723

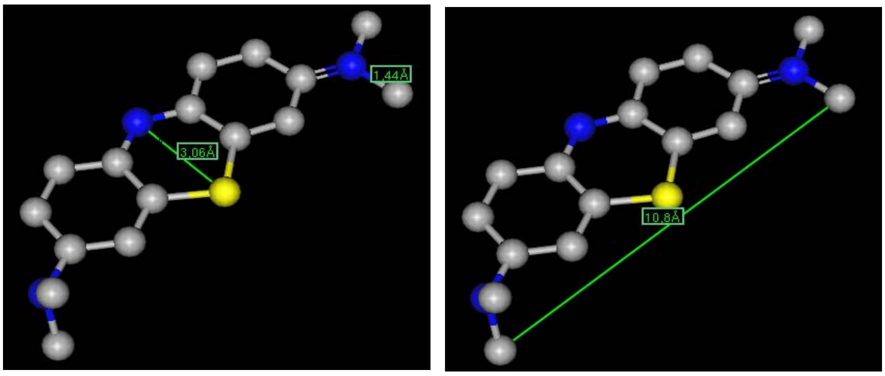


Fig. 4. Spatial structure and intermolecular dimensions of the MB dye

in aqueous solution (distilled water) with MB in the presence of the NaM-AV or NaM-S polyelectrolytes at dye and polyelectrolyte concentrations of: 0.5; 1; 1.5; 2; 2.5%, the solution with *p*H = 5.5- 6 adjusted with 10% acetic acid and a liquor ratio of 1:50. Practically, to the dyestuff aqueous solution of the dyestuff one adds polyelectrolyte in different concentrations and acetic acid - some drops to adjust the *p*H. The dyeing flask is magnetically stirred for 5 min for homogenization and then the solution stays still for 30 min, after which Melana fibres are added (1g). The solution is stirred again for 5 min and then the dyeing flask follows the thermal regime. The dyeing solution is heated up to 80°C and kept at this temperature for about 10 min. The heating continues up to temperatures of 90, 95 or 100°C at a heating rate of 1°C/min. This temperature is maintained for about 75 min , after which the dyeing solution is slowly cooled. The dyed Melana is intensely washed for 5 min with cold water and 5 minutes with warm water, manually squeezed and dried at room temperature. Besides the dyeing operations performed in the presence of the two polyelectrolytes, witness operations of Melana dyeing were also carried out in the absence of the polyelectrolytes at 90°C for 75 min [4].

The spectrophotometry method analysis is used, because it is a precise technique that accurately gives the measurements, formulations and quantitative control of the wanted colour. It measures the reflection of an object on the entire wavelength range afferent to the light spectrum perceivable by the human eye, from 400 to 700nm, exactly specifying each colour [4, 11].

Melana dyed in this way was washed with water, then dried under normal conditions, and the remission values were measured with a portable Datacolor Check plus spectrophotometer at three wavelengths located at 30nm intervals within the range of 400÷700nm. The light source was the D65 illuminant [4].

The spatial images and molecular dimensions of the polyelectrolytes and dyeing stuff were determined by means of the software ChemAcson Marvin Space 5.4.0.0 [4].

Results and discussions

In order to discuss the relation between the chemical structure and the properties of the partners involved in this study, we have calculated the ratios A_3/A_1 and A_3/A_2, which represent a measure of the metachromatic phenomenon intensity, and the ratio A_1/A_2 which is considered a measure of the monomer and dimmer dye in equilibrium; A_1, A_2 and A_3 represent the monomer, dimmer and metachromatic compound absorbances from previously obtained spectra [4-6].

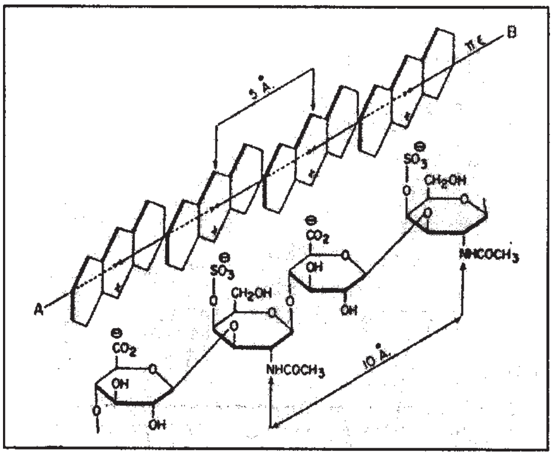


Fig. 5. Suggested model of a metachromatic complex azine dye/polyelectrolyte [4, 15]

The calculated values of the A_3/A_1, A_3/A_2 ratios are considered as a measure of the intensity of metachromatic phenomenon, and A_1/A_2 – a measure of the monomer and dimmer dye in equilibrium, where A_1 is the monomer absorbance, A_2 is the absorbance of dye dimmer and A_3 the absorbance of the metachromatic compound in the case of the NaM-VA/MB system are presented in table 1.

One can see in table 1 that for values of the ratio [P]/[C] =0.1÷0.3, the concentration of MB under monomer form increases simultaneously with the increase of the metachromatic compound concentration. With the increase of the NaM-VA concentration in the system, and of the ratio [P]/[C] =0.5÷1.3, the concentration of MB under monomer form decreases simultaneously with the increasing concentration of MB under the dimmer form and the concentration of the metachromatic compound. When the polyelectrolyte concentration increases, at [P]/[C] ~ 1.3, the system tends toward a state where the dye monomer, the dimmer and the metachromatic compound have the same weight.

Table 2
VALUES OF THE A_3/A_1, A_3/A_2 AND A_1/A_2 RATIOS FOR THE NaM-S/MB IN TERMS OF THE NEUTRALIZATION FACTOR α

No	[NaMS]/[MB]	A_1	A_2	A_3	A_1/A_2	A_3/A_2	A_3/A_1
1	0	-	-	-	-	-	-
2	0.1	1394	846	252	1.648	0.298	0.181
3	0.3	1280	786	297	1.628	0.378	0.232
4	0.5	1083	697	389	1.554	0.558	0.359
5	0.7	839	571	411	1.469	0.720	0.490
6	0.9	697	526	469	1.325	0.892	0.673
7	1.0	590	491	434	1.202	0.884	0.736
8	1.1	571	464	498	1.231	1.073	0.872
9	1.3	446	434	498	1.028	1.147	1.117

Table 3
SPECIFIC WAVELENGTHS OF MB AS A MONOMER (λ_1), DIMMER (λ_2) AND OF THE METACHROMATIC COMPOUND (λ_3)

[Polyelectrolyte]	[Dye]	λ_1, nm	λ_2, nm	λ_3, nm
NaM-VA	MB	664	612	567
NaM-S	MB	664	612	570

Some studies have shown that the configuration of the π electrons of the dye bond to the polyelectrolyte can influence mainly the distance between the positions of polyanion bonding [4].

The MB ions with a thiazine structure (fig. 4) interact mainly by means of the electrostatic forces, with the anionic groups of the NaM-VA, in aqueous solution and get closer to each other, so that they can suffer a multimerization.

This multimerization (polymerization) of the dyes along the polymer chain can be similar to the interaction that occurs in concentrates solutions of the dyestuff and involves two factors: the interaction of the π electrons of the adjacent cations and hydrophobic interaction. The last one is similar to the generation of mycelium in aqueous solutions of anionic detergents [4, 14].

A scheme which renders these processes is found in (fig. 5) showing the interaction between an azine dye with an anionic polyelectrolyte. This model can explain the metachromatic interaction in the NaM-VA/MB and suggest that when the metachromatic dyes polymerize with sharing of π-electrons there occurs branching of the electron gas along the line perpendicular to the planes of the dye molecules which gives rise to a new band at a wave length shorter than that of the dye in its monomeric form [4].

The calculated values of the A_3/A_1, A_3/A_2 ratios are considered as a measure of the intensity of metachromatic phenomenon, and A_1/A_2 – a measure of the monomer and dimmer dye in equilibrium, where A_1 is the monomer absorbance, A_2 is the absorbance of dye dimmer and A_3 the absorbance of the metachromatic compound in the case of the NAM-S/MB system are presented in table 2.

In table 2 one can see that with the [P]/[C] ratio increase, the concentration of the metachromatic compound, and respectively the A_3/A_2 and A_3/A_1 ratios, also increase, simultaneously with the decrease of the concentration of dye monomer and dimmer, and of the A_1/A_2 ratio. Discontinuities on the A_3/A_2 and A_1/A_2 curves can also be noticed within the range of [P]/[C] = 0.9 ÷1.1.

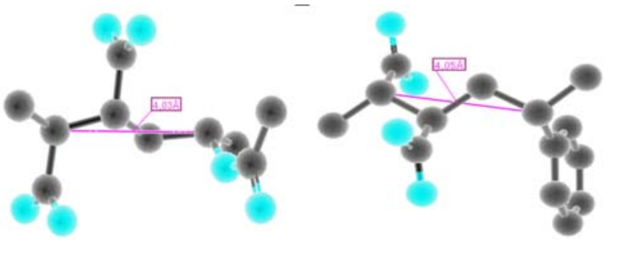


Fig. 6. Spatial structures of the copolymer: a. sodium maleate-vinyl acetate (NaM-VA) and b. sodium maleate- styrene (NaM-S) styrene

The studies concerning the nature of the metachromatic interactions suggest that the spectral shifts are the result of the aggregation of the dye bond, to the charged groups from polyanions. When the polyelectrolyte concentration in the system increases, a redistribution of the dye aggregated to the polyelectrolyte anionic groups occurs, which explains to a certain extent the decrease of dye absorbance from the value A_1 to a minimum value corresponding to the maximum value of the ratio [P]/[C] = 1.3 [1, 2, 4].

In the case of the NaM-S/MB system, one can notice that at a maximum value of the ratio [P]/[C] ~1.3 the three curves are relatively close to each other, which suggests the dye bonding, either as dimmer or as monomer, to the polymer chain. In other words, with the increase of the polylectrolyte concentration, the system tends toward a state in which the dimmer dye, the monomer dye and the metachromatic compound have the same weight.

The metachromasy is a complex phenomenon which implies multiple bonds between the dye and the polyanion. In this situation, the modification of the absorption band in the metachromatic dye spectrum in the presence of the polyelectrolytes is specific for each polyelectrolyte. The increase of the spectral shift occurs when the dye hydrophobic character and/or aggregation tendency increase [4].

The studies concerning the bonding between dyes and polyelectrolytes have shown that three types of interactions are superposed in this case [1-4]:

- the interaction between the ion of the dye molecule and the opposed charge from the polymer chain,
- hydrophobic interaction between dye molecules and non-polar molecules of polyelectrolyte,
- interaction between the π electrons of the adsorbed dye adjacent molecules.

Among these interactions, probably the first one has the bigger influence on the spectral properties of the adsorbed dye, as the π electrons of the dye are directly involved in the light emission and absorption processes.

The amplification of the spectral shift occurs when the hydrophobic character and/or the dye aggregation tendency increase [4]. In table 3 one can notice the difference between the two studied systems in terms of the specific wavelength of the metachromatic compound.

In these cases, the metachromatic band intensity depends on the polyelectrolyte chemical character: NaM-VA determines a relative decrease of the hydrophobia of these systems, due to its moderate hydrophilic character, while NaM-S determines an increase of systems hydrophobic, simultaneously with a relative steric hindrance due to the presence of steric radical. This difference of behaviours is reflected in the balance state between monomer, dimmer and the metachromatic compound [16, 17].

By analyzing the spatial structures of the dye and of the polyelectrolytes from figures 4, 5, 6a and b, one can see that the molecular architecture of the NaM-S/MB metachromatic compound can be much more uniform than in the case of the NaM-VA/MB system, due to the styrene residues from NaM-S, which can control the interaction positions of each MB molecule [4, 18-21

The studies concerning the acrylic fibre dyeing with cationic dyestuffs have shown that the substantivity of the cationic dyestuffs to acrylic fibres is the result of the ionic and hydrophobic interactions between the dyestuff and the fibre. The cationic group of the free dye in solution can turn to the fibre surface to interact with the negative groups, while the hydrophobic segment of the dyestuff can turn to the fibre exterior. In order to obtain uniform dyeings, one must thoroughly control the rate of temperature increase beyond the vitrifying point. When this is not possible, the equalizers are resorted too [4, 24-32].

The anionic retarders interact with dyestuffs, forming a compound with a smaller diffusion velocity inside the solution, therefore a slower sorption. The mechanism of dyestuff bonding to the PAN fibre in retarder presence can be schematically represented as follows [4]:

$$Col^{+} + Ret^{-} \xrightleftharpoons[>80^{\circ}C]{<65^{\circ}C} Col - Ret \qquad (1)$$

$$Col^{+} + PAN^{-} \xrightleftharpoons[>95^{\circ}C]{>65^{\circ}C} Col - PAN \qquad (2)$$

where:

Col^{+} – dyes cation;

Ret^{-} – retarder (polyelectrolyte) anion;

PAN^{-} - free anionic groups from the ends of polyacrylonitrile macromolecular chains.

By slowly heating the dye liquor, the aggregates (1) from the solution, bound through non-ionic (van der Waals, hydrophobic, hydrogen) bonds to the charged positions of the NaM-S polyelectrolyte come apart very easily and turn to the charged positions existing at the ends of the macromolecular chain of Melana fibre (2). While the existing dyestuff aggregates come apart easily, the ionic bonds between the dyestuffs and the polyelectrolyte are hard to break off, due to the strength of the ionic bond and to the styrene residue from the polyelectrolyte structure, which determines a steric hindrance, slowing down the release of the dye cations [1, 4].

As the substantivity of MB cations to the acrylic fibres is high, the reaction with the anionic groups from the extremities of Melana macromolecular chains can be very fast, which results in their dyeing. The presence of NaM-S in the Melana fibres dye liquor determines an increase of the hydrophobia of the whole system. It is very possible that at the anionic groups from Melana fibre macromolecule dye, aggregates are generated, similar to those formed at the anionic positions from the NaM-S or NaM-VA polyelectrolytes (figs. 1, 4) [4].

The Melana fibres were dyed with MB in the presence of NaM-S or NaM-VA through the above presented procedure. The remission data are presented in table 4.

By analyzing the data from table 4, one can notice that the remissions of the Melana samples dyed with MB in the presence of the NaM-VA polyelectrolyte are smaller that those of the standard dyed samples in the visible range of 450÷700 nm. The NaM-VA polyelectrolyte determines the decrease of remission of Melana samples dyed like this. Such modifications can be accounted for by the hydrophilic character and the absence of steric hindrance phenomenon [4, 11].

One can notice that within the wavelength range 450-700 nm the remission values for the Melana fibres dyed with MB in the presence of NaM-S are smaller than those of the standard dyed samples, and the polyelectrolyte induces an acceleration effect on fibre dyeing. The variation of the polyelectrolyte concentration does not determine a significant variation of the remission values of the dyed Melana fibres.

Comparing the data of remission can say that in the case of Melana samples dyed with MB in the presence of NaM-S or NaM-VA, at small wavelength can be accounted for by the difference of hydrophilic-hydrophobic character of the two polyelectrolytes and the steric hindrance due to both the styrene residue from the structure of NaM-S.

From the above data, one can notice a good concordance between the values of the remission for Melana samples dyed with MB in the presence of NaM-VA or NaM-S, and the UV-Vis spectroscopy data, namely [4-6,11]:

- when appropriate absorption band metacromatic complex system is weak NaM-S/MB or NaM-VA/MB values Melana remission samples dyed with MB in the presence of NaM-VA or NaM-S is maximum;

No	λ, nm	Std.	0.5% NaM-S	1.5% NaM-S	2.5% NaM-S	0.5% NaM-VA	1.5% NaM-VA	2.5% NaM-VA
1	400	**42.11**	54.19	56.16	59.40	36.60	36.49	36.39
2	430	**47.16**	46.80	50.03	52.39	41.38	40.98	40.71
3	460	**40.79**	36.71	39.58	40.60	31.42	31.37	31.14
4	490	**34.45**	29.26	31.17	31.98	24.23	24.04	24.15
5	520	**30.72**	26.15	27.05	29.11	21.60	20.5	21.21
6	550	**19.53**	15.16	14.87	16.57	12.22	11.17	11.96
7	580	**10.22**	6.72	6.37	6.89	5.28	4.88	5.26
8	610	**5.66**	3.16	3.26	3.26	2.54	2.54	2.73
9	640	**5.16**	2.78	2.92	2.80	2.31	2.38	2.53
10	670	**4.5**	2.64	2.58	2.69	2.11	2.18	2.28
11	700	**20.32**	13.85	13.69	14.08	11.16	11.17	11.06

Table 4
REMISSIONS DATA OF MELANA FIBRES DYED WITH MB IN THE PRESENCE OF NaM-S OR NaM-VA

No	λ nm	K/S std	K/S 0.5% NaM-S	K/S 1.5% NaM-S	K/S 2.5% NaM-S	K/S 0.5% NaM-VA	K/S 1.5% NaM-VA	K/S 2.5% NaM-VA
1	400	0.396	0.396	0.1711	0.139	0.549	0.552	0.556
2	410	0.318	0.317	0.1773	0.143	0.406	0.405	0.442
3	420	0.287	0.287	0.2079	0.174	0.375	0.380	0.387
4	430	0.296	0.296	0.250	0.216	0.413	0.423	0.432
5	440	0.326	0.376	0.312	0.282	0.502	0.507	0.515
6	450	0.369	0.369	0.378	0.351	0.609	0.611	0.620

Table 5
K/S DATA OF MELANA FIBRES DYED WITH MB IN THE PRESENCE OF NaM-S OR NaM-VA at λ = 400÷450 nm

- when the levels Melana remission samples dyed with MB in the presence of NaM-VA or NaM-S, corresponding metacromatic complex NaM-S/MB or NaM-VA/MB system tends to increase;
- in areas where values Melana remission samples dyed with MB in the presence of NaM-VA and NAM-S are weak bands corresponding metacromatice complex system metacromatic NaM-S/MB, NaM-VA/MB shows maximum intensity;
- when values Melana remission samples dyed with MB in the presence NaM-VA or NaM-S will tend to increase in the bands corresponding metacromatic complex systems NaM-S/MB or NaM-VA/MB tend to decrease.

Moreover, the wettability of NaM-VA polyelectrolyte determines an acceleration of Melana dyeing, while the hydrophobia of NaM-S polyelectrolyte determines the Melana dyeing retarding effect, which accelerates when the steric hindrance phenomenon is present.

In order to establish if the NaM-S or NaM-VA present a retardation effect on the Melana fibres dyeing with MB, we have calculated the values of K/S ratios corresponding to remission within the $400 \div 450$ nm range, where the dye present the maximum absorption (table 5) [4, 11].

At $\lambda \approx$ 436 nm (the region where MB shows maximum absorption), one can notice that only the K/S values corresponding to Melana samples dyed with MB in the presence of NaM-S with concentrations of 1.5% and 2.5%, are smaller than those of the standard samples. The retardation effect exerted by NaM-S in the process of Melana dyeing with Methylene blue is the result of steric hindrance induced by the styrene radical, which retards the release of dye molecules bound through ionic or hydrophobic bonds with the polyelectrolyte from the metachromatic compound, thus producing also a relative dyeing uniformity.

The K/S values corresponding to Melana samples dyed in the presence of NaM-VA are higher than those of the standard sample. The presence of the NaM-VA polyelectrolyte in the system determines an effect of acceleration of the Melana samples dyeing with MB, irrespective of its concentration. Its hydrophilic character and the absence of the steric hindrance phenomenon result in a quick release of dyestuff cations and a non-uniformity of Melana fibre dyeing.

Conclusions

The molecular architecture of the NaM-S/MB metachromatic compound can be much more uniform than in the case of the NaM-VA/MB system, due to the styrene residues from NaM-S, which can control the interaction positions of each MB molecule.

The differences in the remissions data of the system Melana fibres dyed with MB in the presence of NaM-S and NaM-VA can be accounted for by the hydrophobic/hydrophylic character, and the appearance of the steric hindrance phenomenon due to the styrene residue in the NaM-S molecule.

Regarding the values of K/S, hydrophylic character of NaM-VA polyelectrolyte determines an acceleration of Melana dyeing, while the hydrophobia of NaM-S polyelectrolyte determines the Melana dyeing retarding effect, which accelerates when the steric hindrance phenomenon is present.

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