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NEW MALEIC COPOLYMERS USED IN THE PAN FIBRES RESTORATION

SPECTRAL REMISSION MEASUREMENTS

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Abstract

In this study are presented data on the effect of two maleic acid copolymers with styrene (NaM-S) or vinyl acetate (NaM-VA), on Melana fibre dyeing with Methylene blue (MB), Crystal violet (CV) or Victoria Blue B (VBB) and their influence on remission curves. The effect of retardation/acceleration of the two poly-electrolytes (NaM-S, NaM-AV) on Melana fibres dyed in this way were evaluated by calculating K/S ratio values corresponding to the 400÷450 nm range where the three dyes have their maximum absorption peaks.

Keywords: cationic dyes, Melana fibres, retardation effect, acceleration effect, K/S values

1. Introduction

The investigation of the material's properties of the patrimony objects is necessary to understand both the reaction of the objects to the environment in order to create the optimal condition to preserve them and to act on the objects in order to decrease degradation. The specific research on specific materials (textiles, leather, paper, wood) is very important not only for preservation of the patrimony objects but, in addition, to obtain information about their age. For example, in the case of the textile objects, the characteristics of texture, the manufactory, colorants used can be good elements in order to stabilise the age, the provenience and their authenticity [1-3].

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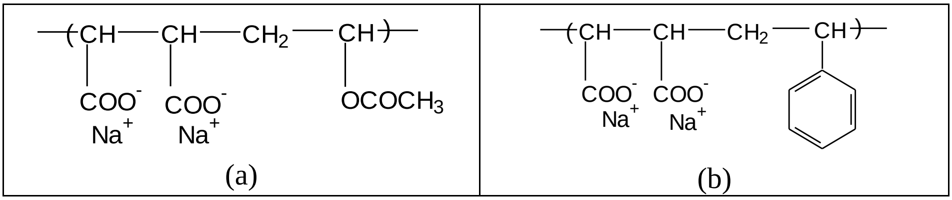
The colour is a sensation perceived as the result of the action of light with different wavelengths on the eye. There is a straight connection between colour and light, since to any luminous sensation corresponds a colour sensation, and light absence excludes colour perception.

In the case of surfaces that do not emit their own light, the colour excitation can not be identified with the illumining radiation, but it becomes a function due to the relation established between incident light and the corresponding body. In order to accurately measure the quantity of light reflected (or remitted) by a surface, one needs to thoroughly specify the illumination and visualization conditions [4, 5].

The used analysis method is spectrophotometry, 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 700 nm, exactly specifying each colour [6, 7].

2. Experimental

The used polyelectrolytes were: a maleic acid copolymer with vinyl acetate NaM- VA (a) and with styrene NaM-S (b), both in the form of natrium salt. The two polyelectrolytes were obtained from the maleic anhydride copolymer with vinyl acetate or styrene, according to the methods described in literature [8]. The chemical structure of the polyelectrolytes is presented in Figure 1.



(a)

(b)

Figure 1. Chemical structures of the copolymers: (a) natrium maleate- vinyl acetate (NaM-AV) and (b) natrium maleate–styrene (NaM-S).

The studied dyes are: Methylene blue AM (a), Crystal violet CV (b) and Victoria blue B AVB (c), Merck reactives utilized as delivered, without purification or other previous modifications. The spatial images of these dyes are presented in Figure 2.

The procedure of Melana fibres dyeing was described in details in [9]. For the analysis of the effect produced be the electrolytes on the Melana fibres dyed with AM, CV or AVB and their influence on remission, we have considered three series of poly-electrolyte concentrations (0.5, 1.5 and 2.5%) and a concentration of the three dyes of 1.5%, constant and identical with that of the Melana samples dyed under standard conditions. The dyeing was always performed at the same dyeing temperature and duration (90°C, 75 min) [10].

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 10 nm intervals within the range of 400÷700 nm. The light source was the D65 illuminant.

3. Results and discussion

The remission data corresponding to Melana fibres dyed with the three dyes (AM, CV and AVB) in the presence of the two polyelectrolytes (NaM-S, NaM-AV) have been processed by using the Excel 97 tabular computing program. The obtained remission values have been graphically represented in terms of wavelength, getting thus four remission curves of the dyed Melana fibres [9].

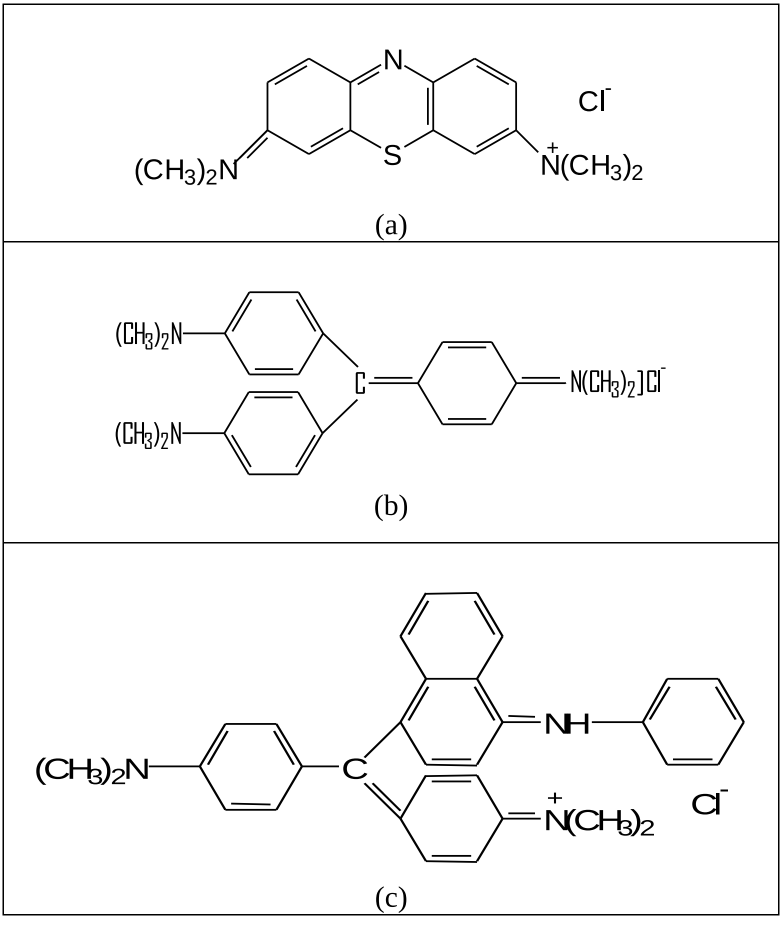


Figure 2. Spatial structures of the dyes: Methylene blue (AM), (b) Crystal violet (CV) and (c) Victoria Blue B (AVB).

Figure 3 presents the remission curves for the system of Melana fibres dyed with Methylene blue in the presence of the polyelectrolytes NaM-S (a), and NaM-AV (b) respectively.

By analysing the remission curves from Figure 3, one can notice that the remission values for the Melana samples dyed with Methylene blue in the presence of NaM-S are superior to the standard within the 400-430-450 nm interval, having an initial descending tendency.

The studies concerning the acrylic fibres dyeing with cation dyers have shown that the cation dyer to the acrylic fibres is due to the ionic and hydrophobic actions between dye and fibre [11]. The cation group of the free dye found in solution can orientate toward the fibre surface in order to interact with the negative groups, and the hydrophobic segment of the dye can turn toward the fibre exterior [12].

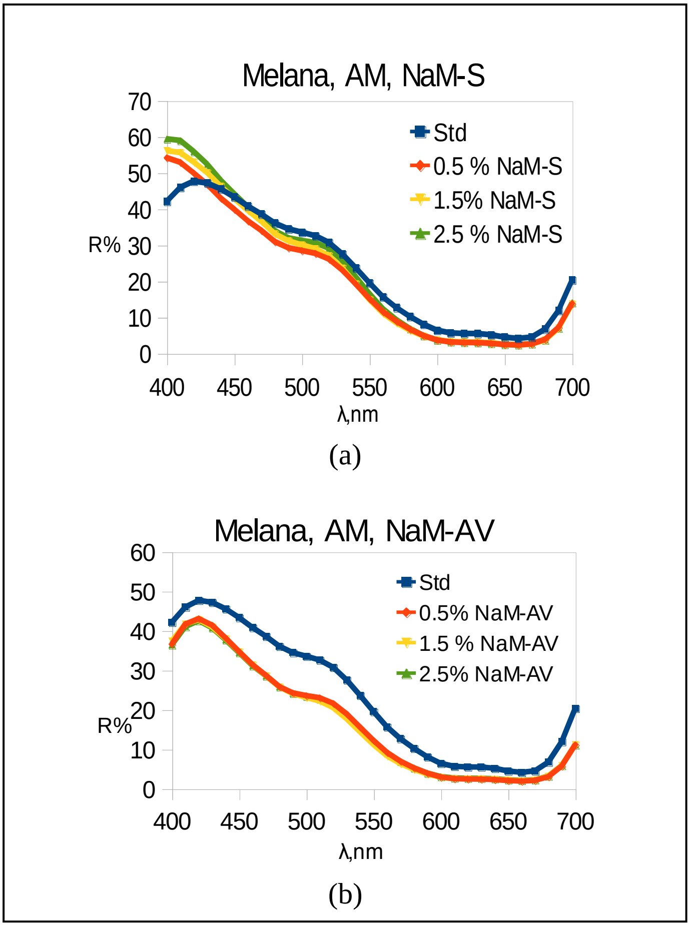
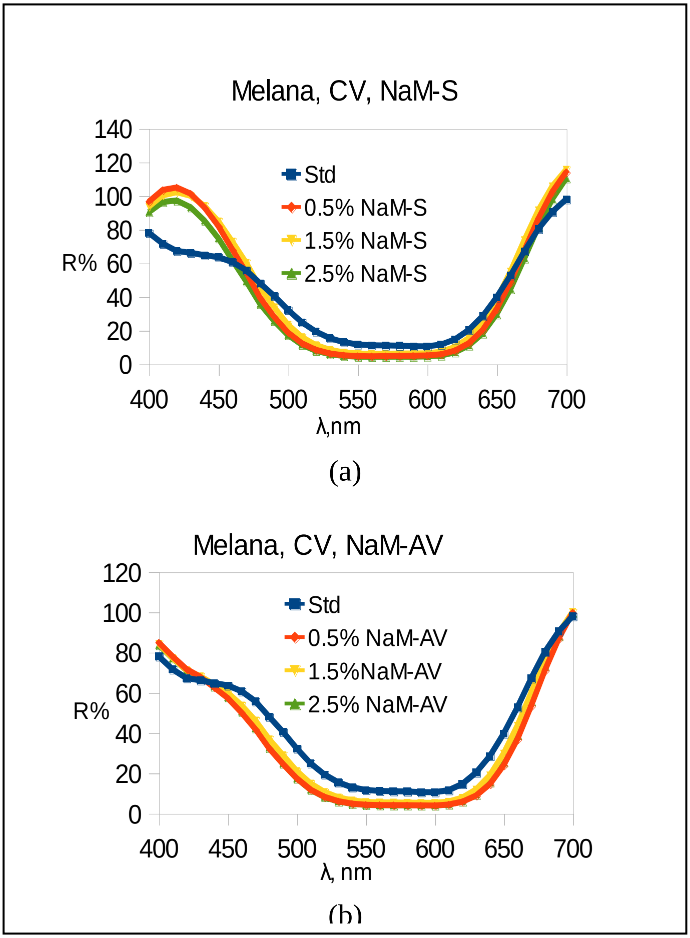


Figure 3. Remission curves corresponding to Melana fibres dyed with Methylene blue, in the presence of polyelectrolytes: (a) NaM-S and (b) NaM-AV.

By a slow heating of the dye liquor, the Methylene blue aggregates from solution bound to the charged sites of NaM-S polyelectrolyte through non-ionic bonds (van der Waals, hydrophobe, hydrogen) break off very easily and turn to the charged sites existing at the ends of the macromolecular chain of Melana molecule [13]. While the existing dye aggregates break off easily, the ionic bonds between dye and polyelectrolyte breaks off more difficult, due to the strength of the ionic bond and of the styrene residues from polyelectrolyte structure, braking thus the dye cation release.



(a)

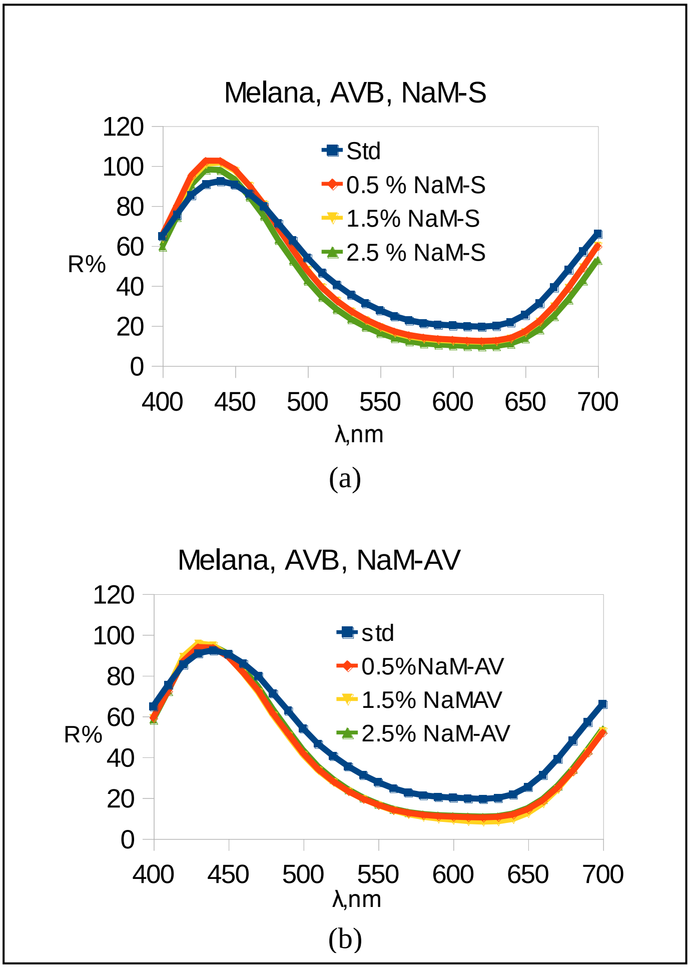
(b)

Figure 4. Remission curves corresponding to the Melana fibre samples dyed with Crystal Violet, in the presence of polyelectrolytes: (a) NAM-S and (b) NaM-AV.

The presence of the NaM-S polyelectrolyte in the Melana fibre dye liquor determines an amplification of the hydrophobicity of the entire system. It is very possible that at the anionic groups from the Melana fibre macromolecule, dye aggregates be generated, similar to those generated at the anionic sites from NaM-S or NaM-AV polyelectrolytes [9]. One can notice that the variation of polyelectrolyte concentration does not induce a significant variation of the remission values of the Melana samples dyed in this way (Figure 3a).

In Figure 3b one can notice an increase of the remission values within the 400÷420 nm wavelength range, which reach a maximum for all the four systems at 420 nm, decreasing then down to 670 nm. Within the 670÷700 nm interval, one can notice a second increase of remission for the three samples until the wavelength of 700 nm.

By comparing the remission curves from Figure 3, we can state that the differences between the aspect of the remission curves of Melana fibres dyed with Methylene blue in the presence of NaM-S and NaM-Av respectively can be accounted for by the different hydrophobic/hydrophilic character, as well as by the presence or absence of steric hindrance phenomenon [14, 15].



(a)

(b)

Figure 5. Remission curves corresponding to the Melana fibre samples dyed with Victoria blue B, in presence of: (a) NaM-S and (b) NaM-AV.

Figure 4 illustrates the remission curves corresponding to the systems of Melana fibres dyed with Crystal violet in the presence of the polyelectrolytes NaM-S (a) and NaM-AV (b) respectively.

One can notice in Figure 4a that within the 400÷470 nm interval, the aspect of the remission curves corresponding to the Melana fibres dyed with CV in the presence of NaM-S polyelectrolyte differs from that of the standard dyed Melana fibres, due to the hydrophoby of the steric radical and the steric hindrance phenomenon which is amplified in this case by the large volume of the Crystal violet molecule.

The triaminotriphenylmethane dyes (for instance Crystal violet) present very marked remission phenomena, such that the colour (greenish) of their crystal is complementary to the colour of the solutions they make (red-violet) [15]. In Figure 4a, one can notice that this phenomenon is amplified at small wavelengths of 400÷470 nm, due to the presence of NaM-S polyelectrolyte.

When analyzing the remission curves from Figure 4b, one can remark that within the 400÷450 nm range, their aspect is different from that from Figure 4a, due to the nucleophylic character of the NaM-AV polyelectrolyte, and the steric hindrance is only the result of the large volume of Crystal violet molecules. In these cases, the differences between the remission curves of Melana fibres dyed with Crystal violet in the presence of NaM-AV and the remission curve of standard dyed Melana fibres is the result of the nucleophylic character of NaM-AV polyelectrolyte.

The aspect of the remission curves in the case of Melana fibres dyed with Crystal violet in the presence of NaM-S or NaM-AV at small wavelength can be accounted for by the difference of hydrophobic/hydrophilic character of the two polyelectrolytes, by the steric hindrance due both to the styrene residue from the NaM-S polyelectrolyte, and to the fact that the triaminotriphenylmethane dyes (Crystal violet, for example) show very marked remission phenomena [15].

Figure 5 illustrates the remission curves corresponding to the Melana fibres dyed with Victoria blue B in the presence of NaM-S polyelectrolyte (a) and NaM-AV (b) polyelectrolyte respectively.

One can notice from Figure 5a that the remission curves of Melana fibres dyed with Victoria blue B in the presence of NaM-S have almost the same shape and tendency of variation as the standard sample within the entire interval of 400÷700 num. The remission values of the dyed Melana fibres insignificantly diminish with the increase of the NaM-S polyelectrolyte concentration. This behaviour can be accounted for by the strong hydrophobia of the dyed Melana fibres, the steric hindrance due to large volume of Victoria Blue B molecule and the presence of styrene residue from the structure of the NaM-S polyelectrolyte [16, 17].

In order to establish if the two polyelectrolytes (NaM-S and NaM-AV) present a retardation effect on the Melana fibres dyeing with Methylene blue, Crystal violet or Victoria blue B, we have calculated the values of K/S ratios corresponding to remission within the 400÷450 nm range, where the three dyes present the maximum absorption, then the K/S values were graphically represented in terms of wavelength [4, 5].

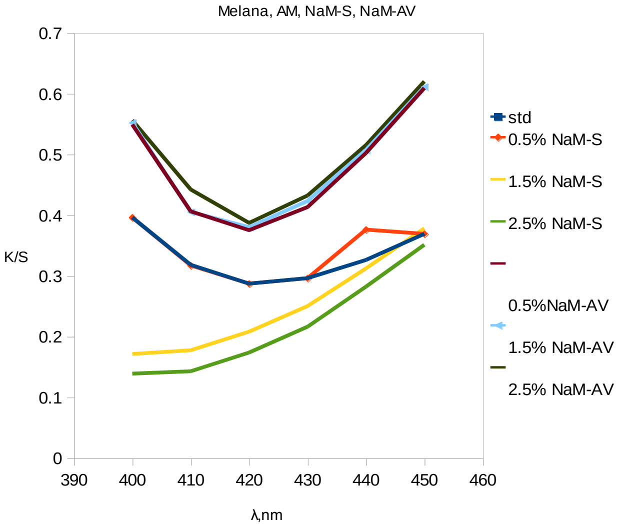


Figure 6. K/S values corresponding to Melana samples dyed with Methylene blue in the presence of the two polyelectrolytes: NaM-S or NaM-AV

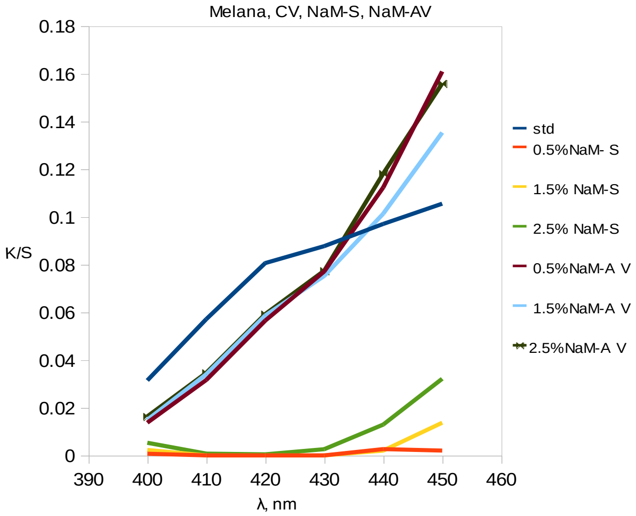


Figure 7. K/S values corresponding to Melana samples dyed with Crystal violet in the presence of the two polyelectrolytes: NaM-S or NaM-AV.

Figure 6 presents these values in terms of wavelength in the case of Melana fibres dyed with Methylene blue in the presence of NaM-S and NaM-AV polyelectrolytes.

At λ ≈ 436 nm (the region where AM shows maximum absorption), one can notice that only the K/S values corresponding to Melana samples dyed with AM in the presence of NaM-S with concentrations of 1.5% and 2.5%, are smaller than those of the standard samples. Therefore, the NaM-S polyelectrolyte (with concentrations ranging between 1.5% and 2.5%) presents a retardation effect during the process of Melana dyeing with Methylene blue.

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 brakes 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.

Also from Figure 6 one can notice that the K/S values corresponding to Melana samples dyed with Methylene blue in the presence of NaM-S 0.5% at λ ≈ 436 nm are bigger than those of the standard dyed Melana samples. In this case, the NaM-S polyelectrolyte presents an accelerating effect on Melana fibres dyeing with methylene blue (possibly due to the concentration diminution in the system).

The K/S values corresponding to Melana samples dyed in the presence of NaM-AV are higher than for the standard ones. The presence of the NaM-AV polyelectrolyte in the system generates an accelerating effect of the Melana sample dyeing with Methylene blue irrespective of its concentration, due to its hydrophilic character and the absence of steric hindrance phenomenon that generates a quick release of dye cations.

The accelerating effect of Melana fibres dyeing process with Methylene blue in the presence of NaM-AV appears due to the easiness with which the dye cations are released from the metachromatic compound, and the real possibilities to react with anionic groups from the ends of Melana fibre chain.

Figure 7 presents these values in function of the wavelength in the case of Melana samples dyed with Crystal violet in the presence of the two polyelectrolytes: NaM-S and NaM-AV.

One can notice in Figure 7 that at λ = 400 nm (the wavelength at which the absorption of Crystal violet dye is maximum), all the K/S values corresponding to Melana fibres dyed with Crystal Violet in the presence of NaM-S or NaM-AV are smaller than that of the standard dyed Melana samples.

Polyelectrolytes NaM-S and NaM-AV present a retardation effect irrespective of the concentration at which they are found in the process of Melana sample dyeing with Crystal violet, due to the large volume of dye molecules and the hydrophobia of these systems. The steric hindrance phenomenon is more pronounced in the case of Melana samples dyed in the presence of NaM-S, due to the styrene radical. This differentiation can be noticed by comparing the K/S values of the systems from Figure 7. Moreover, the K/S values are very small due to the very large remission shown by these Melana samples dyed with Crystal violet [15].

Figure 8 presents these values in function of the wavelength in the case of Melana samples dyed with Victoria blue B in the presence of the two polyelectrolytes, NaM-S and NaM-AV.

One can notice from Figure 8 that at λ = 436 nm (the wavelength at which the absorption of Victoria blue is maximum), the K/S values corresponding to the Melana samples dyed with Victoria blue B in the presence of NaM-S or NaM-AV are smaller than that of the standard dyed Melana samples. In this case too, the NaM-S and NaM-AV polyelectrolytes present a retardation effect irrespective of their concentration.

In these cases, the retardation effect proves to be weaker as compared to that from Figure 7, due to the large volume of the Victoria blue B cations, which induces a pronounced steric hindrance, somehow braking the breaking of the ionic bonds between the dye cations and polyelectrolyte cations, as well as the aggregate generation. By heating the dye liquor, the dye- polyelectrolyte bonds break off, such that each Victoria blue B cation easily migrates toward charged sites from the ends of the macromolecular chain of the Melana fibres, interacting with them.

In Figure 8 one can observe that the K/S values corresponding to Melana samples dyed with Victoria blue B in the presence of the two polyelectrolytes are close to each other, which suggests that the systems hydrophobia (Melana fibre is hydrophobic, AVB molecule is hydrophobic) and steric hindrance takes advantage.

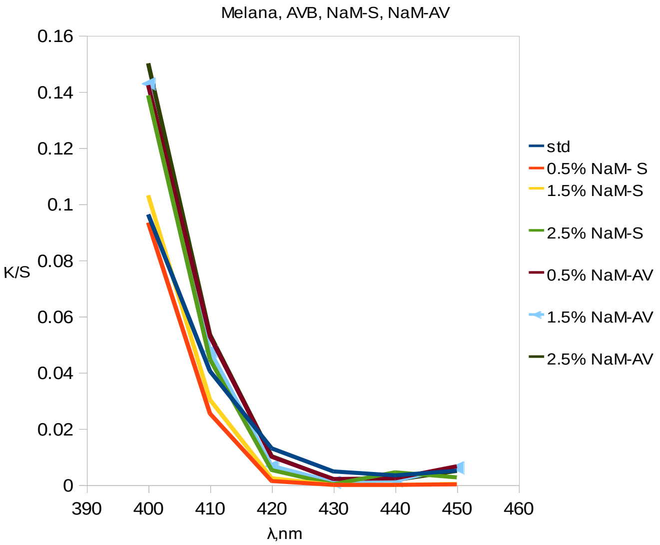


Figure 8. K/S values corresponding to the Melana samples dyed with AVB in the presence of the two polyelectrolytes NaM-S and NaM-AV.

4. Conclusions

The differences in the aspect of remission curves of the system Melana fibres dyed with Methylene blue in the presence of NaM-S and NaM-AV 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.

The aspect of the remission curves in the case of Melana samples dyed with Crystal violet in the presence of NaM-S or NaM-AV at small wavelength is accounted for by the difference of polyelectrolyte hydrophobic/hydrophylic character, the steric hyndrance due to the styrene residue from NaM-S and the fact that the triaminotriphenyl methan dyes show very pronounced remission phenomena.

The remission curves corresponding to Melana fibers dyed with AVB in the presence of NaM-S or NaM-AV have the same shape and the same variation tendency as those of the standard sample within the entire interval of 400÷700 nm.

The K/S values corresponding to the Melana samples dyeing in the presence of NaM-AV are higher than the standard ones. The presence of the NaM-AV polyelectrolyte in the system determines an acceleration effect on Melana sample dyeing with Methylene blue irrespective of its concentration, due to its hydrophilic character and the absence of the steric hindrance phenomenon which determines a quick release of the dye cations.

The NaM-S and NaM-AV polyelectrolytes present a retardation effect irrespective of their concentration in the processes of Melana dyeing with Crystal violet or Victoria Blue B, due to the large volume of dye molecules and the hydrophobia of these systems.

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