

Influence of Anionic Maleic Polyelectrolytes on the Colour Parameters at Dyeing the Melana Types Fibres with Crystal Violet

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The present study pursues the influence of polyelectrolytes based on maleic co-polymers with styrene (NaM-S) and vinyl acetate (NaM-VA) under the form of natrium salt, on the colour parameters CIE L, a*, b* of the Melana-type polyacrylonitrile fibres dyed with Crystal Violet. The colour differences are ascribed to the modifications appeared in the colour components, in terms of concentration, polyelectrolyte character and tinctorial parameters: dyeing duration and temperature.*

Keywords: maleic anionic polyelectrolytes, Crystal Violet, Melana - type polyacrylonitrile fibres, colour parameters CIE L*a*b*

It has been shown that when dyeing the acrylic fibres with cationic dyes, the substantivity of cationic dyes to acrylic fibres is the product of the ionic and hydrophobic interactions between the dyes and the fibre. The cationic group of the free dye in solution can get directed toward the fibre surface in order to interact with the negative groups, while the hydrophobic segment of the dye gets oriented toward the fibre exterior [1].

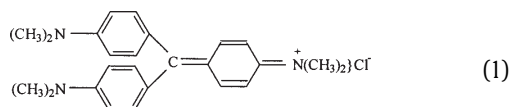
The spectral remission studies on Melana samples dyed with cationic dyes in the presence of maleic polyelectrolytes have shown that the maleic copolymer with styrene (NaM-S) determines a retarding effect in the dyeing process, while the copolymer of maleic acid with vinylacetate (NaM-VA) induces an accelerating effect of dyeing under given conditions [2].

The present study pursued the influence of polyelectrolytes based on maleic co-polymers with styrene and vinylacetate under the form of natrium salt, on the colour difference ΔE of the Melana samples dyed with Crystal Violet. These colour differences are ascribed to the modifications occurred in the colour characteristics L^* , a^* , b^* or L^* , C^* , h^* , depending on polyelectrolyte concentration and character, dyeing time and temperature [3-7].

Experimental part

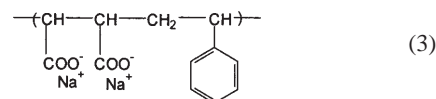
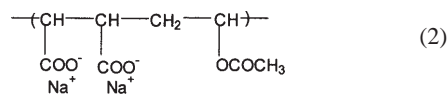
Materials and methods

The studied *dye* was Crystal Violet (CV), Merck reactive, used as such, without purification or other modifications. The dye structure has the following structure:



The utilized *polyelectrolytes* were a copolymer of the maleic acid with styrene (NaM-S) (structure 2) and a copolymer of the maleic acid with vinyl acetate (NaM-VA) (structure 3), both in the form of natrium salt. The two

polyelectrolytes were obtained from copolymers of the maleic anhydride with vinyl acetate or styrene, synthesized in laboratory with methods of our own or described in literature [8-9].



Dyeing methods

The dyeing was performed with a dyeing device Mesdan lab with 6 dyeing positions.

The dyeing (by six dyeing of one gram for each colour position) of Melana fibres was performed in aqueous solutions (distilled water), with AM, in the presence of the polyelectrolytes NaM-VA or NaM-S at dye and polyelectrolyte concentrations of: 0.5; 1; 1.5; 2; 2.5%, the float having a pH of 5.5-6, adjusted with acetic acid 10% and a hydro-module of 1:50. Practically, to the aqueous solution of the dye, one adds polyelectrolyte in different concentrations and some drops of acetic acid to adjust the pH. The dyeing flask is magnetically stirred 5 min for homogenization, and then the solution stays still for 30 min, after which the Melana fibres (1g) are added. The solution is stirred again for 5 min, and then the dyeing flask follows a thermal regime. The dye liquor is heated up to 80°C, being then maintained 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, keeping this temperature constant for 75 min, after which the dyeing solution is cooled slowly. The dyed Melana is washed intensely for 5 min with cold water and 5 min with warm water and then dried at room temperature.

Besides the dyeing performed in the presence of the two polyelectrolytes, witness (standard) dyeing of Melana

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was also performed with AM, in the presence and absence respectively of the two polyelectrolytes at 90°C for 75 min.

The colour differences were measured with a portable Datacolor 2002 spectro-photometer Check Plus [10].

In agreement with [11-14] the colour difference parameters between the (T) sample and that of (R) reference dyes are expressed by the mathematical equations:

$$\Delta a^* = a^*_T - a^*_R; \Delta b^* = b^*_T - b^*_R; \Delta L^* = L^*_T - L^*_R \quad (4)$$

Based on these equations the *deviation* or *chromatic shifting* can be calculated, as the geometrical distance between two positions in the CIE LAB colour space, as follows:

$$\Delta E^* = [\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}]^{1/2} \quad (5)$$

where ΔL^* indicates any difference in brightness and is denoted by + if the sample which reproduces is lighter (brighter) than the witness specimen, and by - if it is darker than this.

The values Δa^* and Δb^* indicate the differences between the positions of the specimens in the chromatic diagram. Thus, „a” represents the chromatic shift to red for positive values, and a shift to green for negative values. Similarly, for the coordinate b, the positive values indicate yellow colours, and the negative ones- blue colours the higher is the chromatic intensity, the bigger will be the numerical value [7].

Then, by using the values of the L^* , a^* and b^* parameters, the following parameters can be calculated:

- the saturation or purity difference, through the relation

$$\Delta C^* = [a^{*2}_T + b^{*2}_T]^{1/2} - [b^{*2}_R + L^{*2}_R]^{1/2} \text{ and} \quad (6)$$

- The tint difference, through the relation (7):

$$\Delta H^* = [\Delta E^{*2} - \Delta L^{*2} - \Delta C^{*2}]^{1/2} \quad (7)$$

The obtained data were processed by means of the tabular program Excel 97 in order to produce the graphical representations of the parameters CIE $L^* a^* b^*$.

Results and discussions

For the interpretation of colour modifications considered to be the result of the poly-electrolytes action, of the dyeing time and temperature on Melana dyed with methylene Blue, the chromatic diagram CIE $L^* a^* b^*$ was used [10].

Table 1 presents the technological parameters and the values of the colour components obtained at dyeing of Melana with CV in the presence of NaM-S or NaM-VA at different polyelectrolyte concentrations.

In the case of Melana dyeing with CV in the presence of polyelectrolytes NaM-S or NaM-VA, modifications of sample colour can be noticed, highlighted by the values of colour difference ΔE at different concentrations of the two polyelectrolytes. For instance, a concentration of 0.5% NaM-S corresponds to a maximum value of $\Delta E = 45.62$, and a concentration of 2.5% NaM-VA corresponds to a maximum value of $\Delta E = 28.56$. With increasing concentration of the two polyelectrolytes to 1.5%, the values of colour difference decrease, yet, this value of ΔE renders evident the polyelectrolyte action in the dye liquor. One can notice from the table 1 that the ΔE values in the case of (CV, Melana, NaM-S) system are higher compared to those of the (CV, Melana, NaM-VA) system. This distinction is due to the chemical character of the two polyelectrolytes”: NaM-S which, besides the relative steric hindrance induced by the presence of the styrene radical from its structure, also determines an increase of the dye liquor wettability, and NaM-VA-its nucleophilic character determining a diminution of the dye liquor hydrophobia and implicitly a poorer dyeing of Melana samples.

The values of the colour differences increase with the increase of the concentration of the two polyelectrolytes to 2.5% in the dye liquor. This might be explained as follows: with the slow heating of the dye liquor, the aggregates of cationic dye from the solution increase and break off, and the dye ions interact with the charged positions of the polyelectrolyte by means of the ionic bonds. Given the high hydrophobia of these systems, non-ionic van der Waals, hydrophobic hydrogen bonds can be generated between fibre, dye and polyelectrolytes [15, 16].

The triaminotrifenilmethane dyes (for example Crystal Violet) present significant remission phenomena, so that the colour of their crystals (greenish) is complementary to the colour of the solutions that they form (red-violet). This very marked remission phenomenon can be compared with the hypsochromic effect, unexpected in the case of the accumulation of the auxochrome groups recorded at the absorption of the Crystal Violet light, which is due to the dye molecule symmetry (structure 3) that provides the common electronic system around the central carbon atom. In consequence, some energetic quantum states are identical, their number decreases and the difference between the ground energy state and the excited energy states are reflected in the light absorption at smaller wavelengths; thus appears the hypsochromic effect noticed in the spectra [17, 18].

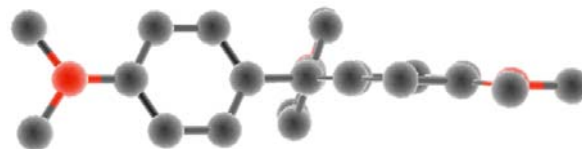


Fig. 1. Planar space orientation of the Cristal Violet molecule

Table 1
TECHNOLOGICAL PARAMETERS AND THE VALUES OF COLOUR COMPONENTS AT DYEING THE MELANA FIBRES WITH CV IN THE PRESENCE OF NaM-S OR NaM-VA AT DIFFERENT POLYELECTROLYTE CONCENTRATIONS

No.	Conc AM (%)	Conc NaM-S (%)	t min	T (°C)	Chroma C* (AN)	Hue h* (°)	ΔL^* (%)	Δa^* (AN)	Δb^* (AN)	ΔC^* (AN)	Δh (°)	ΔE^* (AN)
	C_{CV}	C_{NaM-S}										
Wit.	1.5	0	75	90	57.24	292.34						
1	1.5	0.5	75	90	99.24	303.9	-9.31	33.6	-29.42	42.0	15.19	45.62
2	1.5	1.5	75	90	90.65	302.13	-6.38	26.45	-23.82	33.4	12.29	36.16
3	1.5	2.5	75	90	96.35	303.83	-11.06	31.89	-27.09	39.11	14.87	43.28
	C_{CV}	C_{NaM-VA}										
Wit.	1.5	0	75	90	57.24	292.34						
1	1.5	0.5	75	90	74.62	298.83	-9.43	14.22	-12.42	17.37	7.40	21.11
2	1.5	1.5	75	90	70.63	297.46	-6.80	10.05	-9.93	13.39	5.12	15.67
3	1.5	2.5	75	90	80.62	300.88	-12.91	19.62	-16.24	23.38	10.12	28.56

Certain studies concerning the dyes aggregation have shown that the dimer structure of the CV molecules is very probable in solutions, due to its flexibility, symmetry and flatness. The figure 1 presents a dimer structure proposed in the case of Crystal Violet ions in aqueous solution [16, 19-22].

In figure 1 one can notice that the two Crystal Violet molecules are overlapped only along *one arm*, which determines a shift in the dimer absorption band. This shift is influenced by the conjugation of the non-participant electrons of the auxochrome groups with π electrons or the aromatic rings.

The dimer structure presented in figure 2 shows a high degree of freedom of the molecule. The dimer structure of CV can be influenced by the character of its partners in the dye liquor: the NaM-S polyelectrolyte-hydrophobic character, with a relative steric hindrance due to the steric radical which induces a relatively ordered organization of the CV monomers or dimers toward the positions with the charge from the polyelectrolyte, a fact which does not happen in the care of hydrophilic NaM-VA polyelectrolyte [9, 23-25].

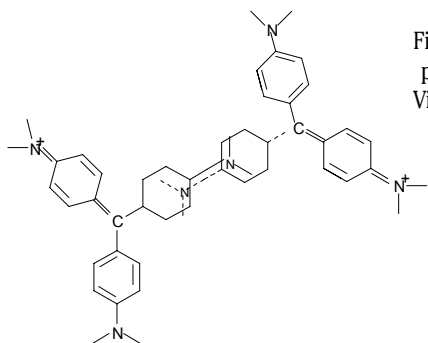


Fig. 2. Dimer structure proposed for Crystal Violet ions in aqueous solutions

The variation of the colour chromatic parameters CIE L^* , a^* , b^* renders evident a modification of the nuance ($\lg b^*/a^*$) and saturation ($C^* = (a^{*2} + b^{*2})^{1/2}$) respectively, as illustrated in figures 1-3 [3].

In figure 3 one can notice that the brightness of Melana samples dyed with Crystal Violet in the presence of the two polyelectrolytes with concentration of 0.5% are lower than those of the standard samples. With the increase of the polyelectrolyte concentration, the brightness values tend upward and, at the maximum polyelectrolyte concentration in the dye liquor (2.5%), these values significantly decrease. The brightness values of the Melana samples dyed with CV in the presence of NaM-S are very close to those of Melana samples dyed with CV in the presence of NaM-VA (fig. 3a).

In figure 3b one can see that the values of a^* are positive in the case of Melana fibre dyed with Crystal Violet in the presence of the two polyelectrolytes. The values of a^* corresponding to Melana samples dyed in the presence of the NaM-S polyelectrolyte are higher than those of the samples dyed in the presence of NaM-VA polyelectrolyte,

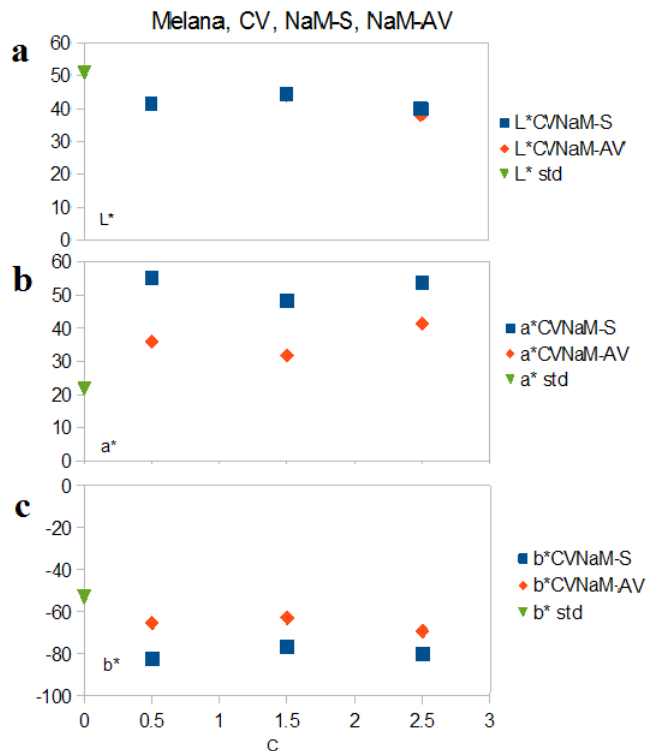


Fig. 3. Influence of the concentration of the NaM-S and NaM-VA polyelectrolytes on the colour parameters of the Melana fibre dyed with Crystal Violet: a - L^* ; b - a^* and c - b^*

such that the Melana samples dyed in the presence of NaM-S are redder than those dyed in the presence of NaM-VA. The Melana samples dyed with Crystal Violet in the presence of the two polyelectrolytes are redder than the witness sample. With the increase of the concentration of the two polyelectrolytes, the values of a^* decrease at first (up to the concentration of 1.5%) and then tend upward when the polyelectrolyte concentration increase to 2.5%.

The values of b^* corresponding to Melana samples dyed with Crystal Violet in the presence of NaM-s and NaM-VA polyelectrolytes are negative (fig. 3c), smaller than those corresponding to the witness sample. The saturation of sample colour increases in this case, and they are more blue than the witness sample. This fact is the result of the high hydrophobia of the entire system due to the hydrophobia of Melana fibres, CV molecules and NaM-S polyelectrolyte. The Crystal Violet molecular organization can be in turn influenced by the relative steric hindrance induced by the styrene radical from the NaM-S composition. One can not exclude the possibility that these colour modifications are only of metachromatic nature [2].

Table 2 presents the technological parameters and the values of the colour components obtained at Melana dyeing with CV in the presence of NaM-S or NaM-VA at different dyeing intervals.

Nr	Conc. AM (%)	Conc. NaM-S (%)	T (min)	T (°C)	Chroma C*	Hue h*	ΔL^* (%)	Δa^* (AN)	Δb^* (AN)	ΔC^* (AN)	Δh (°)	ΔE^* (AN)
wit	1.5	0	75	90	57.24	292.34						
1	1.5	1.5	30	90	92.29	301.93	-5.81	27.06	-25.38	35.05	12.16	37.55
2	1.5	1.5	75	90	90.65	302.13	-6.38	26.45	-23.82	33.4	12.29	36.16
3	1.5	1.5	120	90	97.86	304.91	-15.01	34.25	-27.3	40.61	16.4	46.3
wit	1.5	0	75	90	57.24	292.34						
1	1.5	1.5	30	90	76.75	299.74	-11.39	16.20	-13.76	19.51	8.44	24.11
2	1.5	1.5	75	90	70.63	297.46	-6.80	10.05	-9.93	13.39	5.12	15.67
3	1.5	1.5	120	90	76.71	299.87	-11.98	16.45	-13.57	19.46	8.71	24.46

Table 2
TECHNOLOGICAL PARAMETERS AND THE VALUES OF THE COLOUR COMPONENTS DURING MELANA FIBRES DYEING WITH AM IN THE PRESENCE OF NaM-S OR NaM-VA WITH DIFFERENT DYEING DURATIONS

In figure 4 one can notice that with increasing dyeing time appear colour modifications of Melana fibres dyed with Crystal Violet in the presence of the two polyelectrolytes (NaM-s or NaM-VA), rendered evident by the values of the colour difference ΔE . For instance, at $t = 75$ minutes, the colour differences are minimum: $\Delta E = 36.16$ for the system (Melana, CV, NaM-S) and $\Delta E = 15.67$ for the system (Melana, CV, NaM-VA), and the biggest variations of ΔE correspond to the maximum dyeing time $t = 120$ min (table 2).

The brightnesses of Melana samples dyed with Crystal Violet in the presence of the NaM-S and NaM-VA polyelectrolytes are positive and smaller than those of the witness sample (fig. 4a). These values decrease with the increase of the dyeing time in the case of Melana samples dyed in the presence of the NaM-S polyelectrolyte and increase at first with increasing dyeing time in the case of NaM-VA polyelectrolyte up to $t = 75$ min and NaM-VA conc. of 1.5%. One can notice a brightness diminution for the samples dyed in the presence of NaM-VA polyelectrolyte at a concentration of 2.5% (table 2).

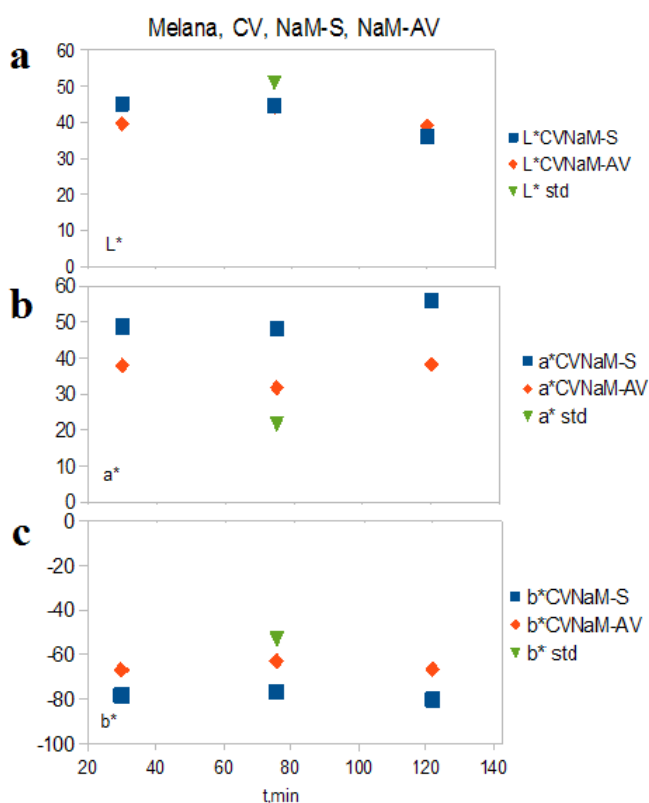


Fig. 4. Influence of the dyeing time on the colour parameters of Melana samples dyed with Crystal Violet in the presence of NaM-S and NaM-VA polyelectrolytes: a - L^* ; b - a^* and c - b^*

The values of a^* (fig. 4b) corresponding to Melana fibres dyed with Crystal Violet in the presence of NaM-S or NaM-VA polyelectrolytes are positive, bigger than those of the witness sample, tending to increase with increasing dyeing time in the presence of the NaM-S polyelectrolyte. In the presence of the NaM-VA, the values of a^* (fig. 4b) decreases at first with the increase of the dyeing time from 30 to 75 min., tending upward when the dyeing time increases from 75 to 120 min. The values of a^* corresponding to Melana fibres dyed with Crystal violet in the presence of NaM-S are bigger than for those dyed in the presence of NaM-VA, and the colour of these samples is redder than that of the witness sample.

The values of b^* corresponding to Melana fibres dyed with Crystal Violet (fig. 4c) in the presence of NaM-S or NaM-VA polyelectrolytes are negative and bigger than that of the witness sample, the samples being more blue than the witness sample [13]. One can notice that the values of b^* corresponding to Melana fibres dyed with Crystal Violet in the presence of NaM-VA are smaller as compared to NaM-S case.

The increase of dyeing temperature determines colour alterations in the samples of Melana dyed with Crystal Violet in the presence of the two polyelectrolytes (table 3), expressed by the values of the colour difference ΔE . For instance, at maximum dyeing temperature of 100°C , colour differences reach a maximum of 45.83 corresponding to the system (Melana, CV, NaM-S) and of 30.63 in the case of (Melana, CV, NaM-VA) system.

Table 3 presents the technological parameters and the values of colour components obtained at dyeing Melana with CV in the presence of NaM-S or NaM-VA at different dyeing temperatures.

Colour differences of the Melana samples dyed with Crystal Violet in the presence of NaM-S or NaM-VA is reflected in the variations of the colour components L^* , a^* , b^* .

In the case of Melana fibres dyed with Crystal Violet in the presence of the NaM-S and NaM-VA polyelectrolytes, the sample brightness decreases with temperature increase from 80 to 100°C (fig. 5a). The brightness values of Melana fibres dyed according to standard or in the presence of the two polyelectrolytes are very close to each other.

The figure 5b shows that the values of a^* in the case of Melana fibres dyed with Crystal Violet in the presence of the NaM-S and NaM-VA polyelectrolytes are positive and increase with the increase of dyeing temperature from 80 to 100°C . The values of a^* corresponding to Melana fibres dyed with Crystal Violet in the presence of the NaM-S are bigger than of those dyed in the presence of NaM-VA, which are bigger than those of witness samples. Melana samples dyed with Crystal violet in the presence of the NaM-S are redder than those dyed in the presence of NaM-VA.

In figure 5c one can notice that the values of b^* are negative in the case of Melana fibres dyed with Crystal

No	Conc AM (%)	Conc NaM-S (%)	t (min)	Temp ($^\circ\text{C}$)	Chroma C* (AN)	Hue h* ($^\circ$)	ΔL^* (%)	Δa^* (AN)	Δb^* (AN)	ΔC^* (AN)	Δh ($^\circ$)	ΔE^* (AN)
wit	1.5	0	75	90	57.24	292.34						
1	1.5	1.5	75	80	70.16	296.71	11.37	9.78	-9.72	12.92	4.84	17.87
2	1.5	1.5	75	90	90.65	302.13	-6.38	26.45	-23.82	33.4	12.29	36.16
3	1.5	1.5	75	100	98.13	304.37	-13.47	33.64	-28.06	40.89	15.71	45.83
wit	1.5	0	75	90	57.24	292.34						
1	1.5	1.5	75	80	56.58	291.62	2.18	-0.91	0.35	-0.66	-0.72	2.39
2	1.5	1.5	75	90	70.63	297.46	-6.80	10.05	-9.93	13.39	5.12	15.67
3	1.5	1.5	75	100	79.67	301.49	-17.88	19.86	-14.99	22.42	10.78	30.63

Table 3
TECHNOLOGICAL PARAMETERS AND THE VALUES OF THE COLOUR COMPONENTS DURING MELANA FIBRES DYEING WITH AM IN THE PRESENCE OF NaM-S OR NaM-VA AT DIFFERENT DYEING TEMPERATURES

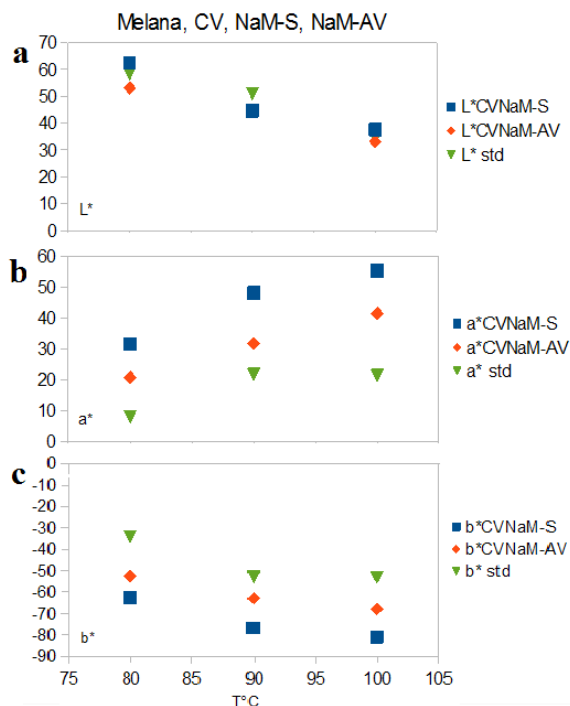


Fig. 5. Influence of the dyeing temperature on the colour parameters of Melana fibres dyed with Crystal Violet in the presence of the NaM-S și NaM-VA polyelectrolytes: a - L*; b - a* and c- b*

Violet in the presence of the NaM-S or NaM-VA polyelectrolyte. With the increase of the dyeing temperature from 80 to 100°C, the values of b* tend downward and Melana fibres dyed with Crystal Violet in the presence of the NaM-S or NaM-VA are coloured in a more intense blue than the standard dyed samples. The values of b* corresponding to Melana fibres dyed with Crystal Violet in the presence of the NaM-VA are smaller than for Melana fibres dyed with Crystal Violet in the presence of the NaM-S, these samples being coloured in a more intense blue.

Conclusions

During Melana dyeing with Crystal Violet in the presence of the maleic anionic polyelectrolytes (NaM-S or NaM-VA) colour alterations occur, whose intensity depends on the concentration and character of the two polyelectrolytes and on the tinctorial parameters: dyeing duration and temperature.

Colour differences ΔE of the Melana fibres dyed with Crystal Violet in the presence of the NaM-S or NaM-VA are reflected in variations of colour components L, a*, b*.

The brightness of the Melana samples dyed with Crystal Violet in the presence of the NaM-S or NaM-VA are smaller than those of the Melana samples dyed in the absence of polyelectrolytes, irrespective of the variations of the tinctorial parameters.

With the increase of the polyelectrolyte concentration or dyeing duration, the values of a* corresponding to Melana dyed with Crystal Violet in the presence of NaM-S are bigger than of those dyed in the presence of the NaM-VA, which are bigger than those of the witness sample. Melana samples dyed with Crystal Violet in the presence of the NaM-S are redder than those dyed in the presence of NaM-VA.

With the increase of the polyelectrolyte concentration or of the dyeing duration, the values of b* tend downward, the saturation increases and the Melana samples dyed with Crystal violet in the presence of the NaM-S or NaM-VA

polyelectrolyte are more blue than the witness samples. The values of b* corresponding to Melana samples dyed with Crystal violet in the presence of the NaM-VA polyelectrolyte are smaller than those of the Melana samples dyed with Crystal Violet in the presence of the NaM-S, these samples being more blue.

The values of a* and b* parameters increase with the increase of the dyeing temperature, and the influence of the two polyelectrolyte character is „cast into shade”.

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