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Thermodynamic and kinetic parameters of polyester dyeing with Disperse Blue 56 using biobased auxiliaries and co-solvent microemulsion

Abstract

The study aims to dye a polyester fabric with a low molecular weight anthraquinone type disperse dye (C.I. Disperse Blue 56), n-butylacetate as co-solvent in the microemulsion system and the presence of two bio based auxiliaries (o-vanillin and coumarin) at temperatures lower than 100°C. In order to investigate the influence of the temperature and the aforementioned auxiliaries on the kinetic dyeing process, the energy of the activation by the kinetic rates constants were determined. The activated entropy by the theory of absolute rates of dyeing and diffusion of the activated state of the dye for the disorder state of the dyeing system were obtained. Higher activated energies, and higher activated entropy so higher dye absorption for polyester samples dyed with o-vanillin/n-butylacetate than polyester samples dyed with coumarin/n-butylacetate were found. Color strength values of the polyester fabric dyed for this proposed micro-emulsion dyeing system at low temperature (95°C) and the polyester fabric dyed with conventional dyeing system at high temperature (135°C) were similar. According to color fastness to washing and ironing, it was found that the use of these auxiliaries did not modify the fastness values of the dyed samples significantly.

Keywords: Polyester, dyeing kinetic, apparent activation energy, coumarin, o-vanillin, n-butylacetate, microemulsion dyeing

1. Introduction

The kinetic dyeing microemulsion system of the polyethylene terephthalate (PET) with disperse dyes at lower temperatures than conventional dyeing process with the co-solvent (n-butylacetate) were studied previously [1,2].

In this sense due to growing environmental concerns, there has been significant interest in dyeing polyester with carriers or additives at lower temperatures, considering their biodegradability, low toxicity and environmentally friendly practices [1-3].

With the aim of saving water and energy, Gao et al, 2018 proposed an environmentally friendly dyeing process, using silicone nanomicelle technique, which the organic silicone oil was used as nano-emulsion by solvent evaporation, this technique improved the dyeability of the polyester compared to polyester dyed by the traditional dyeing system which requires more energy consumption [4].

Parvinzadeh Gashti and Moradian, 2011 prepared PET/Clay nanocomposite via melt spinning system, and the study confirmed that the presence of the clay on polyester increased the dyeability of the polyester by reducing the glass transition temperature of the PET. This method avoids the disadvantages of the toxic carriers [5].

Additionally, Parvinzadeh Gashti et al, 2015 modified the surface of the polyester by corona discharge ionization process. The Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and reflectance spectroscopy (RS) proved that the corona discharge improved the surface functionality and dyeability of the polyester [6].

Pasquet et al. 2013 dyed polyester fabric with o- and p-vanillin in the presence of two disperse dyes (C.I Disperse Blue 56, and C.I Disperse Blue 79) with ethanol as co-solvent. The study confirmed that color strength of the polyester dyed with these auxiliaries was good, mainly when o-vanillin was used [7].

Radei et al [2,3] proposed the use of two alternative bio-based auxiliaries such as ortho-vanillin (o-vanillin) and coumarin with n-butylacetate as a co-solvent, in the microemulsion system for the high molecular disperse dyes (C.I. Disperse Blue 79 and Disperse Red 167) [3]. This new proposed microemulsion system has advantages such as using biodegradable and non-toxic auxiliaries during the dyeing process. Furthermore, the dyeing system is favorable from both economic and environmental point of view. The microemulsion system is formed with micro particles containing the co-solvent, the dyes and the auxiliaries used, and these micro particles including the dye molecules facilitate the transport to the fiber in function of the temperature used [3,8]. Many studies have been done on kinetics and thermodynamic parameters of polyester dyeing processes in the equilibrium state; however, there is a lack of data related to the thermodynamic parameters before the equilibrium state for improvement the exhaustion and levelness during the kinetic dyeing process [9-11].

The aim of this paper is to study the dyeing process of a polyester fabric with a low molecular weight anthraquinone type disperse dye (C.I. Disperse Blue 56), with n-butylacetate as co-solvent (low environmental impact) in the microemulsion system and the presence of two bio based auxiliaries (o-vanillin and coumarin) at temperatures lower than 100°C. In order to investigate the influences of the temperature and the aforementioned auxiliaries on the kinetic dyeing process, the energy of the activation by the kinetic rates constants were obtained. The activated entropy was calculated by the theory of absolute rates of dyeing and diffusion in the activated state. This entropy was obtained by rate kinetic and diffusion dyeing values, such were obtained by other authors [12; 13, 14]. The theory of absolute rates of dyeing has advantages for explanation of absorption kinetic dyeing system in the activated state. The quality of the dyed fabrics was evaluated by determining color fastness to ironing and washing.

2. Experimental

2.1 Materials

2.1.1. Fabric

A standard plain-woven 100% polyester fabric, Type 30 A, from Testgewebe GmbH (Germany) (ISO 105-F10) was used as textile substrate. The average fiber diameter of the fabric was 10 μ .

2.1.2 Chemicals and auxiliary products

Antraquinone type low molecular weight disperse dye Foron Blue E-BL supplied by Archroma GmbH (Germany) (C.I. Disperse Blue 56, $M_w = 365.18 \text{ g}\cdot\text{mol}^{-1}$) was used as a dye. As a co-solvent pure n-butylacetate from Panreac (Spain) (boiling point 126 °C) was used. Coumarin ($M_w = 146.15 \text{ g}\cdot\text{mol}^{-1}$) and o-vanillin ($M_w = 152.15 \text{ g}\cdot\text{mol}^{-1}$) with 99% purity supplied by Acros (USA) were used as bio-based auxiliaries, respectively. The chemical structure of the co-solvent, the disperse dye and the two selected auxiliaries are indicated in Figures 1, 2, 3 and 4 respectively.

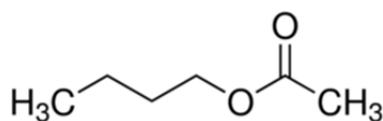


Figure1. n-butylacetate, CAS NO. 123-86-4

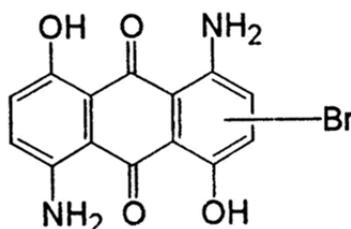


Figure 2.C.I. Disperse Blue 56, CAS NO. 12217797

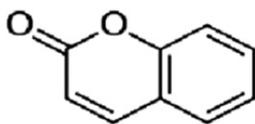


Figure 3. Coumarin (2H-chromen-2-one), CAS No. 91-64-5

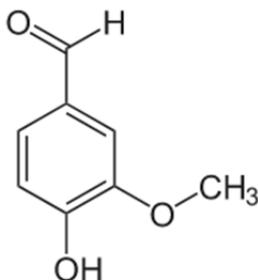


Figure 4. O-vanillin (2-hydroxy-3-methoxybenzaldehyde), CAS No. 148-53-8

Hostapal NF liq a non-ionic surfactant supplied by Archroma was used for the pre-dyeing washing. Eganal RAP liq supplied by Archroma (Germany) as a dispersing agent was used. Sodium hydrosulphite ($MW = 174.11 \text{ g}\cdot\text{mol}^{-1}$) and analytical-grade sodium hydroxide, both supplied by Panreac, were used for the post reductive washing. N,N-Dimethylformamide (DMF) with 99.8% purity supplied by Panreac (Spain) was used to extract the dyestuff from the fabric.

2.2. Isothermal dyeing procedure

The dyeing procedure was performed as described by Radei et al. 2018. The standard polyester fabrics were pre-washed (40 °C for 30 minutes) with 2 g/L of Hostapal NF liq, then rinsed with distilled water and dried at room temperature. Afterwards, fabrics were dyed with 2% o.w.f of disperse dye, 4% o.w.f. of auxiliaries (o-vanillin or coumarin) and 16.66 g/L of n-butylacetate as a co-solvent. Bath ratio was fixed at 1:60. An isothermal dyeing process was performed at four temperatures (65, 75, 83 and 95 °C) for 120 minutes, except for the lower temperature (65 °C), which the time was 150

minutes. The dyeing process was performed in a Linitest MTT dyeing machine, Atlas MTT GmbH (Germany).

Post reductive washing was done to remove the adsorbed dye at the surface with 0.5 g/L of sodium hydroxide and 2 g/L of sodium hydrosulphite in distilled water (bath ratio 1:50) at 50 °C for 30 min, followed by rinsing three times with cold distilled water, and drying at room temperature for 24 h. Figure 5 shows an Scheme of the experimental procedure followed in this research.

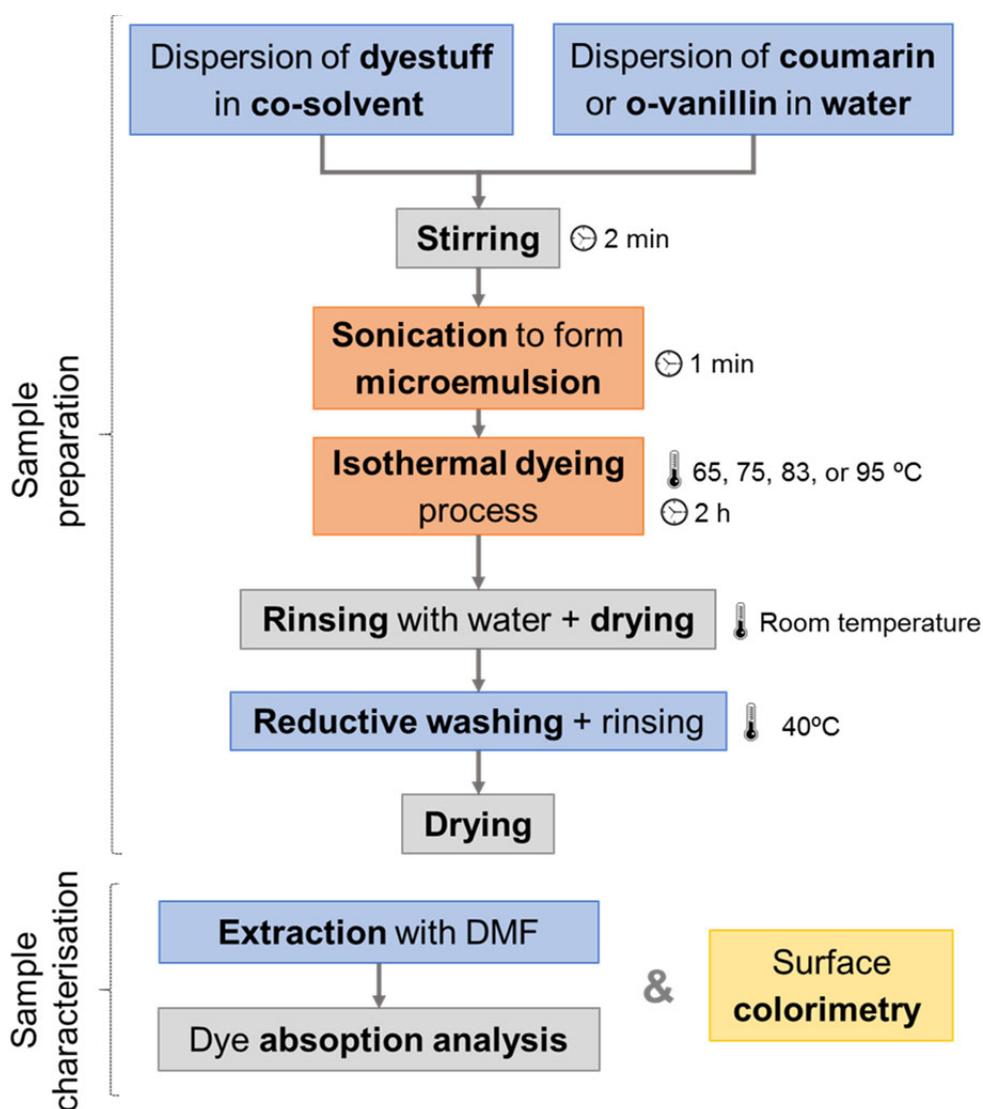


Figure 5. Scheme of the procedure for low dyeing temperature dyeing polyester

2.4. Particle size measurement

Average values of dye baths particle size were determined with a Zetasizer nano series (Malvern, UK) device at 90° with respect to the incident laser beam at 25 °C. Quartz cells 1 cm thick and volume of 4 mL were used.

2.5. Dye absorption measurement

Dye absorbed by the dyed polyester fabric was determined via extraction with DMF. Maximum absorbance was measured at $\lambda_{\max}=640$ nm for C.I Disperse Blue 56. A model M 330 UV–Visible spectrophotometer Camspec (UK) was used.

The equation (1) shows the linearity of the Beer-Lambert law for C.I. Disperse Blue 56 at different concentrations related to their maximum absorbance [15].

$$(\text{Abs})_{\lambda_{\max} 640\text{nm}} = 15.383[D_f] \quad (1)$$

where D_f is the dyestuff concentration in the fiber (mg dye/g fiber) and $(\text{Abs})_{\lambda_{\max} 640\text{nm}}$ is the maximum absorbance . The correlation coefficient was $R^2 = 0.9982$

Experimental values for the amount of the dye extracted from fiber during the kinetics dyeing process were calculated based on the equation 1.

2.6. Colorimetric curves analysis

Colorimetric curves were determined using a spectrophotometer Datacolor SF600 plus-CT. The values were obtained from the average of four individual measures rotating 90° the fabric measured, the illuminant D65, and observer 10° were used.

2.7. Differential scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) tests performed on a Perkin Elmer DSC 7 to determine changes on thermal characteristics of dyed samples. 4mg samples were heated from 40°C to 300°C at a heating rate was 20°C/ min.

2.8. Color fastness

The color fastness to ironing was analyzed according to the UNE-EN ISO 105-X11 method, at three temperatures (110, 150 and 200°C).

Color fastness to washing was tested according to the UNE-EN ISO 105-C06 standard using A2S test stated in the standard. Dyed polyester samples were washed with ten steel balls with and IEC 60456 Base Detergent Type A 2g/L at 40°C for 30 min, bath ratio was 1:50. ATLAS LAUNDER-OMETER GmbH (Germany) was used for the washing test, with a vessel of 550ml.

3. Results and Discussion

3.1. Solubility parameters of auxiliaries, co-solvent, water and polyester used

To study whether the auxiliaries used have the capacity to penetrate inside the fabric, solubility parameters (cohesion energy parameters) were calculated for polyester, o-vanillin, and coumarin with water as the main solvent and n-butylacetate as the co-solvent.

The classic Hansen's formula (equation 2) for solubility parameters was used, where the total parameter is broken down into contributions from the forces involved [16,17].

$$\delta t^2 = \delta d^2 + \delta p^2 + \delta h^2 \quad (2)$$

In which δ_d , δ_p and δ_h are the contributions from dispersion forces, polar forces, and hydrogen bonding respectively.

The total solubility parameter and the contributions from dispersion forces, polar forces, and hydrogen bonding for auxiliaries, co-solvent, water, and polyester at 25°C are shown in table 1.

Table 1. Solubility parameters obtained from the Hansen equation for the auxiliaries, co-solvent, water, and polyester for total dispersion forces, polar forces, and hydrogen bonding, respectively at 25°C.

Sample	δ_t (MPa) ^{1/2}	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}
Polyester	17.9	9.8	9.2	11.8
o-vanillin	24.4	19.4	9.8	11.2
coumarin	24.5	20	12.5	6.7
n-butylacetate	17.4	15.8	3.7	6.3
water	47.8	15.5	16	42.3

Based on total solubility parameters, n-butylacetate has the capacity to diffuse inside the polyester and is insoluble in water. Moreover, o-vanillin and coumarin are partially soluble in the co-solvent used, therefore to form a microemulsion system the dye-bath was prepared by ultra-sonic agitation.

3.1.2. Solubility parameters of auxiliaries in the water

To determine hydrophobic or hydrophilic characteristics of the two auxiliaries used, their solubility parameters in the water were found. Solubility parameter values in the water are 1.7 g/L and 10 g/L for coumarin and o-vanillin respectively, which indicates higher hydrophobicity in the case of coumarin [18.19].

3.2. Particle size measurement

Before the dyeing process each microemulsion system was controlled with particle size analysis. The obtained average values are presented in Table 2.

Table 2. Average particle diameter and polydispersity of the dye-bath prepared

Dye-bath	Average diameter (nm)	Polydispersity
0.333 g/l of Disperse Blue 56 0.666 g/l of coumarin 16.66 g/l n-buthylacetate	269.33 ± 3.6	0.249 ± 0.009
0.333 g/l of Disperse Blue 56 0.666 g/l of o-vanillin 16.66 g/l n-buthylacetate	262.33 ± 6.57	0.238 ± 0.012

The particle size of the dye into stable microemulsion particles are similar in presence of both auxiliaries used, at similar polydispersity, but slightly higher values were obtained in presence of coumarin-

3.3. Dyeing kinetics

The Kinetics for the two microemulsion dyeing systems, at four temperatures and at different times was studied in the presence of o-vanillin or coumarin in n-butylacetate. In table 3, Figures 6 and 7 the values of the dye concentration inside fiber and exhaustion % are shown respectively.

Table 3. Values of C.I. Disperse Blue 56 dye concentration inside the fiber at the studied temperatures in function of time.

		Time (min)								
Temperature		5	10	30	50	70	90	105	120	150
Auxiliary products										
4.556 x 10 ⁻³ mol.	mg dye /g fiber	4.62	6.18	8.10	8.20	9.53	9.71	—	10.52	11.01

L ⁻¹ of coumarin 16.66 g. L ⁻¹ of n-butylacetate	(65 °C)									
	mg dye /g fiber (75 °C)	4.63	6.96	7.65	10.09	11.40	11.46	11.58	12.32	—
	mg dye /g fiber (83 °C)	7.72	10.29	13.86	14.66	15.20	15.82	17.30	18.16	—
	mg dye /g fiber (95 °C)	7.74	8.01	13.90	15.18	16.04	16.93	18.26	19.26	—
Auxiliary products										
4.377 x 10 ⁻³ mol. mol. L ⁻¹ of o- vanillin 16.66 g. L ⁻¹ of n-butylacetate	mg dye /g fiber (65 °C)	2.29	3.23	8.56	8.73	10.48	10.67	—	11.59	11.69
	mg dye /g fiber (75 °C)	5.32	7.02	10.08	10.99	12.34	13.94	16.08	16.67	—
	mg dye /g fiber 83 °C	8.74	9.33	12.59	13.14	16.20	16.41	18.12	18.77	—
	mg dye /g fiber at 95 °C	11.39	14.49	16.49	17.27	18.27	19.12	19.36	19.50	—

It should be noted that the thermodynamic state of equilibrium has not been reached in this dyeing system, as the dyeing time and the amount of the dye-bath were not infinite; therefore, the maximum theoretical concentration (C_{∞}) is 20 mg dye/ g of fiber for 100% of exhaustion

In general, based on the Table 3, it was observed that, o-vanillin led to higher dye concentration (mg dye/g of fiber) in the fiber than coumarin, and also a higher initial dyeing rate. When the microparticles of the disperse dye, the co-solvent and the auxiliaries are in collision with the surface of the fiber, the free dye molecule in the o-vanillin/n-butyl acetate system is more easily deposited on the fiber surface with greater exhaustion than the coumarin/n-butyl acetate system. **The microparticles of the microemulsion collide with the fiber surface and depending on their different instability into the bath system they facilitate more or less their absorption kinetics and consequently the diffusion of the dye. Due to higher hydrophilicity of o-vanillin/bath system, its miroemulsioned particles (i.e. dye molecules) are deposited more easily than on the coumarin/bath system, which is more hydrophobic. The facility of the deposition of the free dye molecules on the surface of the fiber (a hydrophobic solid) after break the microparticle promotes its kinetic absorption and followed diffusion.**

The highest value of dyestuff inside the fiber (mg dye/g of fiber) was obtained for polyester dyed in presence of o-vanillin at 95 °C reaching after 2 hours of dyeing 19.5 mg dye/g of fiber (which means an exhaustion of 97.5%).

In Figures 6 and 7 the values of exhaustion with respect to the time at the temperatures studied are shown. As it can be seen C.I. Disperse Blue 56 for the microemulsion system of o-vanillin/n-butylacetate led to higher exhaustion level than microemulsion system of coumarin/n-butylacetate for the isotherms at temperatures of 75°C, 83°C and 95°C. For both cases, as expected, the absorption isotherm at 65°C led to lower exhaustions.

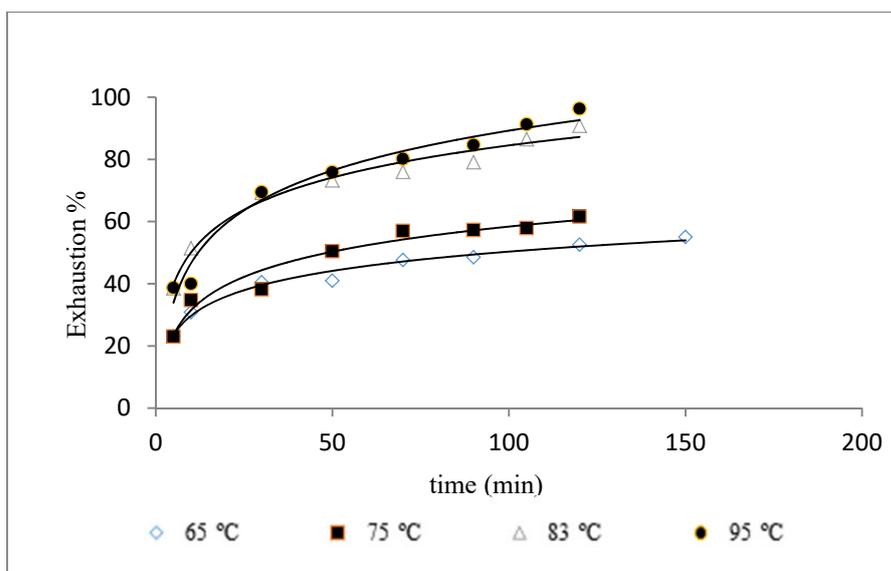


Figure 6. Absorption isotherms of exhaustion in function of time of C.I. Disperse Blue 56 in the coumarin/n-butylacetate microemulsion system at four temperatures.

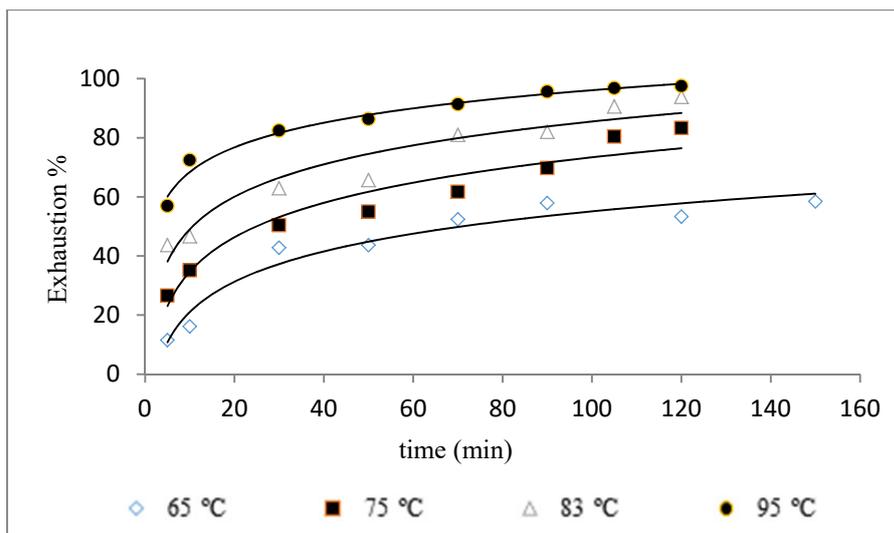


Figure 7. Absorption isotherms of exhaustion in function of time of C.I. Disperse Blue 56 in the o-vanillin/n-butylacetate microemulsion system at four temperatures.

In Figure 8 the microscopic images of the cross-section of the polyester samples dyed in presence of coumarin/co-solvent or o-vanillin/co-solvent compared with the one dyed without auxiliaries are shown.

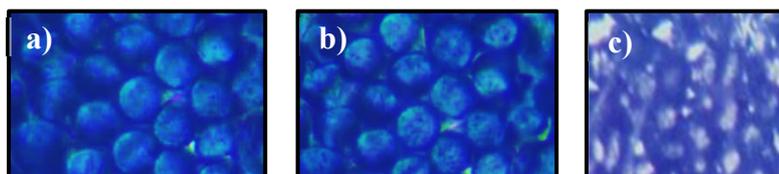


Figure 8. Microscopic images of the cross-section of the polyester fabrics: a) dyed with coumarin/co-solvent at 95 °C during 120 minutes; b) dyed with o-vanillin/co-solvent auxiliaries at 95 °C during 120 minutes and c) dyed without auxiliaries at 95 °C during 120 minutes

As it can be seen, the use of auxiliaries led to a significantly better diffusion to the dye. The dyestuff was uniformly distributed into the fibers, demonstrating the efficiency of the dyeing process presented in this research.

3.5. Efficiency of the microemulsion dyeing process with respect a conventional process

To demonstrate the efficiency of the dyeing process, colorimetric curves of the polyester fabrics dyed with o-vanillin and co-solvent at 95 °C after 120 minutes were compared with the ones obtained with the same fabric subjected to a conventional dyeing process at 95°C and 135 °C in presence of 2 g/L of dispersing agent Eganal RAP. All dyed samples were washed with a post reductive washing as was described on Figure 5. The obtained colorimetric curves are presented in Figure 9.

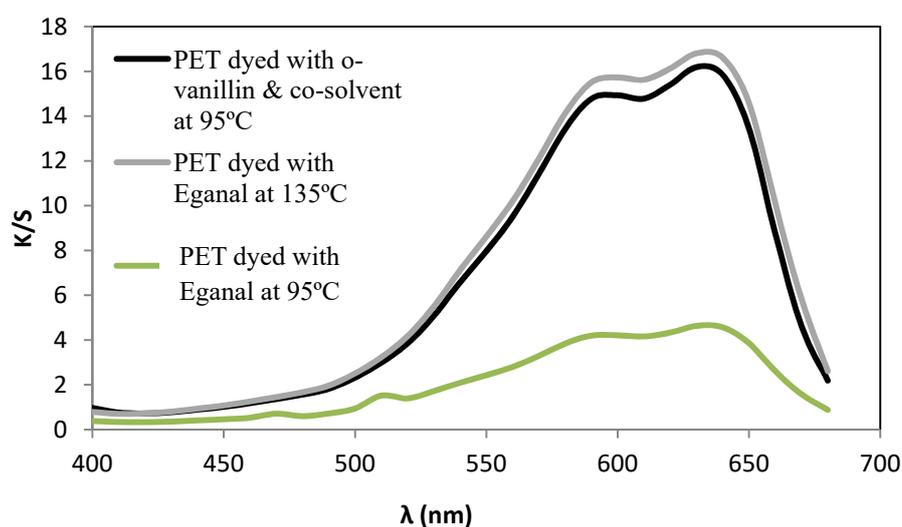


Figure 9. K/S reflectance curves in function of wavelength for the polyester fabrics dyed polyester fabrics dyed with o-vanillin and co-solvent at 95 °C after 120 minutes and the ones obtained with the same fabric subjected to a conventional dyeing process at 95°C and 135 °C in presence of 2 g/L of dispersing agent Eganal RAP.

As shown in Figure 9, the microemulsion system at 95°C led to similar results of K/S to the conventional dyeing at 135°C. However, the conventional system at 95°C led to significantly lower color strength. As shown in Table 4, there is no significant

difference on the K/S values at the maximum wavelength and exhaustion for the microemulsion system at 95°C and the conventional system at 135°C.

Table 4. K/S values at $\lambda=630$ nm, exhaustion percentage and photographic images of the polyester fabrics dyed with o-vanillin and co-solvent at 95 °C after 120 minutes and the ones obtained with the same fabric subjected to a conventional dyeing process at 95°C and 135 °C in presence of 2 g/L of dispersing agent Eganal.

Dyeing time=120 minutes	K/S ($\lambda=640$ nm)	Exhaustion (%)	Photographic image of the dyed fabrics
PET dyed with Disperse Blue 56 and in presence of o-vanillin in n-buthylacetate at 95 °C (microemulsion system)	16.20	97.5	
PET dyed with Disperse Blue 56 and in presence of Eganal at 135 °C (conventional system)	16.81	99.1	
PET dyed with Disperse Blue 56 and in presence of Eganal at 95 °C (conventional system)	4.63	29.1	

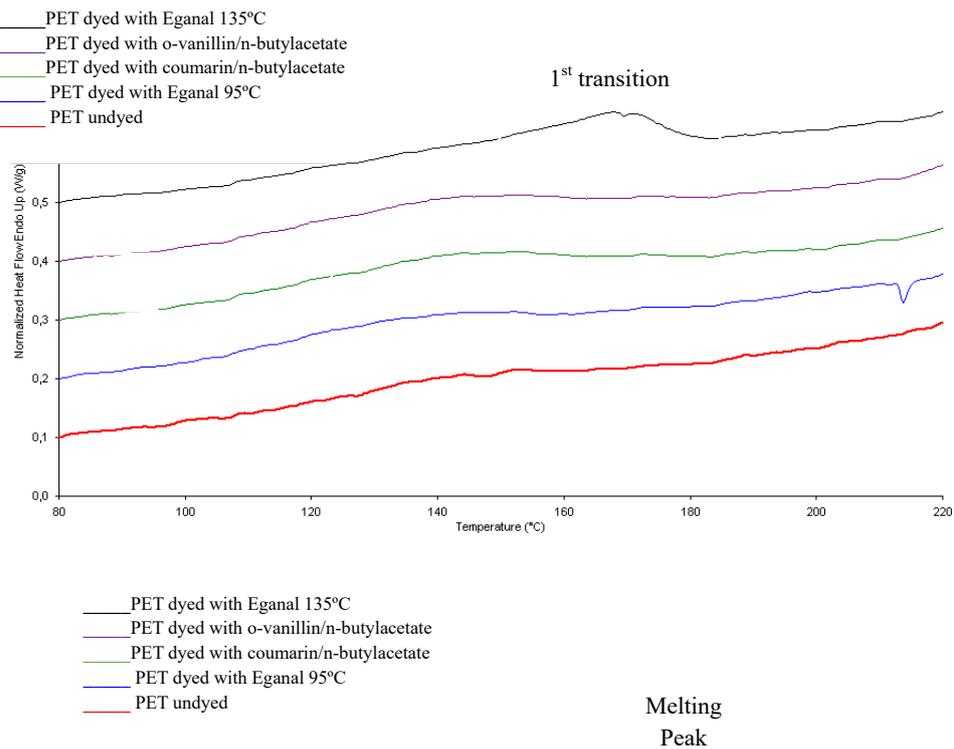
From these results, it can be concluded that the dyeing process presented in this paper (using a co-solvent/o-vanillin at 95 °C) gives color strength similar to a conventional process at 135°C, after the reductive washing, in both cases. This means that with this new process it is possible to reach 97.5% exhaustion with only a slight color difference with respect to the dyeing process at 135 °C, with a reduction of the dyeing temperature by 40°C.

This new system allows saving thermal energy and makes it possible to perform the dyeing process in open equipment and, in the case of dyeing blended fibers,

significantly reduces the risk of damaging the fibers with low resistance to high temperature. These facts demonstrate that the process presented can be appropriate for industrial applications and can be a green alternative method for the industry.

3.6. Differential Scanning Calorimetry (DSC) analysis

In Figure 10 the DSC curves of the dyed fabrics with o-vanillin/co-solvent at 95 °C, with coumarin/co-solvent at 95 °C, compared with the ones dyed with the conventional system at 95°C and 135°C and the undyed fabric. The parameters obtained from these curves are presented in Table 5.



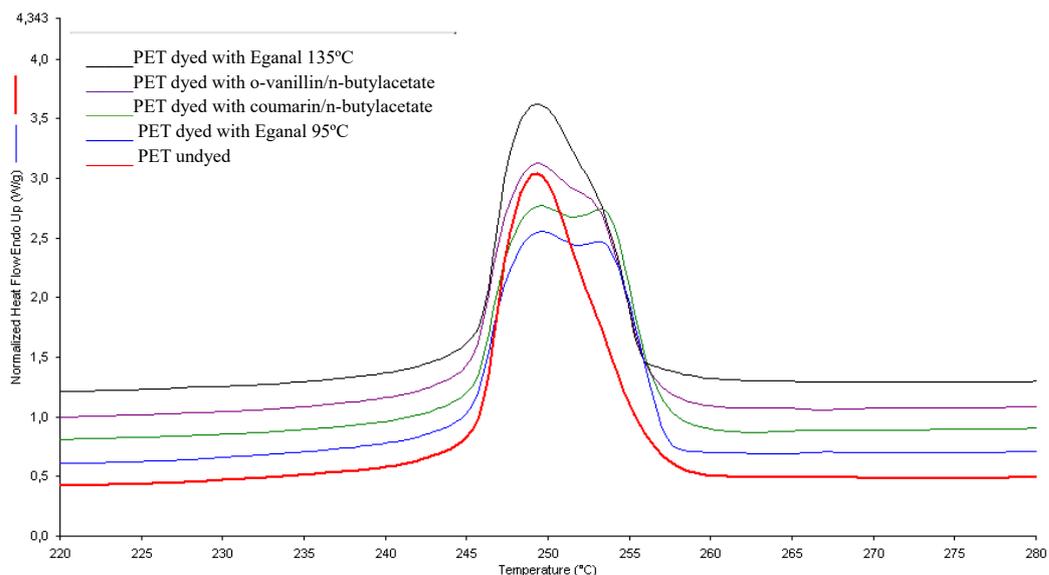


Figure 10. DSC endotherms of the of the dyed fabrics with o-vanillin/co-solvent at 95 °C, with coumarin/co-solvent at 95 °C, compared with the ones dyed with the conventional system at 95°C and 135°C and the undyed fabric: top) zone from 80°C to 220°C and down) zone from 220°C to 280°C.

Table 5. DSC parameters of undyed polyester and polyester samples dyed in different conditions.

Parameters	Original white sample	Conventional dyeing at 95 °C	Dyed with coumarin/co-solvent at 95 °C	Dyed with o-vanillin/co-solvent at 95 °C	Conventional dyeing at 135 °C
Thermal transition 1 ΔH (J/g)	3.234	5.216	7.524	6.280	6.688
Melting peak ΔH (J/g)	61.092	57.645	57.528	57.392	58.067

As indicated in Table 5 and Figure 9, in general, the presence of o-vanillin and coumarin did not modify significantly the thermal characteristics of the dyed fabrics and the co-

solvent is responsible for changes on the microstructure of the fiber. Regarding the first thermal transition (Figure 10a), which is ascribed to a premelting endothermic peak, the conventional dyeing system without auxiliaries at 95 °C and 135°C gives an enthalpy of 5.2 J/g of 6.7 J/g respectively. This means that an increase of 40 °C in the dyeing temperature increased the enthalpy of this transition around 28.2%. Comparing the polyester dyed with conventional system without auxiliaries at 95 °C to polyester dyed with auxiliaries at 95 °C it was observed that the enthalpy of this first thermal transition increases around 44% in the case of the coumarin, and by 20% in the case of the o-vanillin, as indicated before this reveals that n-butylacetate affected on the microstructure of the dyed fibers.

Based on the melting peak, as shown, the dyeing treatments have not significantly modified the enthalpy and the maximum temperature of the melting peak. The only observed changes are on the shape of the endotherm, which is wider for the dyed samples. This is related with changes on the crystals formed as a consequence of the hydrothermal dyeing treatment.

3.7. Thermodynamic parameters

Since in this work is intended to obtain the influence of temperature in the dyeing process of microemulsified dispersed dyes in the presence of the biobased auxiliaries studied at temperatures below 100°C, values of dyeing rate constant, apparent activation energy, apparent diffusion coefficient, enthalpy and entropy for the polyester samples dyed have been calculated by the theory of absolute rates of dyeing and diffusion of the activated state of the dye molecule [12-14].

3.7.1. Dyeing rate constant

To calculate the dyeing rate constant from the initial exhaustion values presented in Table 3, equation 3 was used [20,21]

$$\frac{x}{(1-x)^2} + 0.5 \ln \frac{(1-x)}{(1+x)} = kt \quad (3)$$

where x is the quotient between the dye concentration on the fiber in time t and the initial dye concentration in the dye-bath (C_t/C_∞), k is the dyeing rate constant, and t is the time [22]. The values of the dyeing rate constants calculate from the linearity adjustment of the equation 3 are shown in Table 6.

Table 6. Absorption rate constant (k) for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate at 65 °C, 75 °C, 83 °C, and 95 °C.

	coumarin	o-vanillin
T (°C)	k (min ⁻¹)	k (min ⁻¹)
65	0.0148	0.0139
75	0.0282	0.1077
83	0.1859	0.7654
95	0.3207	5.6561

As expected, the dyeing rate constant increased as the dyeing temperature increased and generally, except for 65°C, values of the dyeing rate constant obtained for the polyester dyed with o-vanillin were considerably higher than the values obtained for the polyester dyed with coumarin. Significantly highest value of dyeing rate constant was obtained at 95 °C for polyester dyed with o-vanillin. This is related with a very fast kinetic dyestuff absorption in all studied times and after 120 minutes of dyeing process, the absorption of dyestuff in the fiber was almost reached to the maximum theoretical concentration.

3.7.2. Apparent activation energy

The apparent activation energy of the dyeing process was calculated from the Arrhenius Law, indicated in logarithm form in equation 4 [23].

$$\ln k = \ln k_0 - \frac{E}{RT} \quad (4)$$

where k is the dyeing rate constant, k_0 is the pre-exponential factor (slope of the line), E is the apparent activation energy, T is the absolute temperature and R is the constant of ideal gases. Values of apparent activation energies obtained from the linear adjustment of equation 4 are shown in the Table 7.

Table 7. Values of apparent activation energy for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate.

Polyester dyed with CI Disperse Blue 56, coumarin/ n-butylacetate		Polyester dyed with CI Disperse Blue 56, o-vanillin/ n-butylacetate	
Activation Energy (Kcal·mol ⁻¹)	Correlation coefficient	Activation Energy (Kcal·mol ⁻¹)	Correlation coefficient
25.34	0.9383	51.05	0.9879

As shown in Table 7, the values of apparent activation energy obtained for polyester dyed with o-vanillin/n-butylacetate is higher than polyester samples dyed with coumarin/n-butylacetate. This is because polyester dyed with o-vanillin/butylacetate during the absorption kinetic process was more influenced by the variation of the temperature; with higher value of activation energy than coumarin/n-butylacetate [24]. Values are almost in the same ranges to those previously achieved in the polyester dyeing at equilibrium [22].

3.7.3. Apparent diffusion coefficient

In order to determine the apparent diffusion coefficient, Crank's equation was used (equation 5) [25, 26].

$$\frac{C_t}{AC_\infty} = 2\left(\frac{D.t}{\pi}\right)^{0.5} \quad (5)$$

where C_t is the concentration of dye inside the fabric in the examined time by using the kinetic equation (3), C_∞ is the maximum theoretical concentration inside the fabric, t is the time examined, D is the apparent diffusion coefficient and A is the specific surface area (per gram) of the studied fiber. The specific surface using the equation 6 was obtained.

After surface divided by weight and after simplification for using μ such as diameter of fiber, following equation was applied for obtaining the specific surface area of the fiber.

$$A = \frac{4 \times 10^4}{\rho \cdot d} \quad (6)$$

Where s is the perimeter of 1 g. length (cm), w is the 1 g. weight (g), ρ is density (cm^3/g) and d (applied in μ) is the diameter of the studied fiber respectively.

Values of apparent diffusion coefficients obtained from the equation (5) are shown in the Table 8.

Table 8. Apparent diffusion coefficients for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate

Apparent diffusion coefficient (D) ($10^{-11} \text{ cm}^2/\text{sec}$)			
Disperse Blue 56	T (°C)	Polyester dyed with CI Disperse Blue 56, coumarin/ n-butylacetate	Polyester dyed with CI Disperse Blue 56, o-vanillin/ n-butylacetate
	65	0.765 ± 0.04	0.531 ± 0.16
	75	0.923 ± 0.04	1.241 ± 0.44
	83	1.833 ± 1.24	2.216 ± 1.41
	95	2.072 ± 0.98	3.775 ± 2.85

As expected, apparent diffusion coefficients increased with increasing temperature. Moreover, polyester samples dyed with o-vanillin lead to higher diffusion coefficients than coumarin/n-butylacetate at all of the temperatures studied. The highest diffusion coefficient was found for polyester dyed in presence of o-vanillin at 95 °C. According to the definition of diffusion coefficient of the activated dye molecule, it can be concluded that the dyestuff penetration in the polyester samples dyed with o-vanillin is faster compared to the polyester samples dyed with coumarin/n-butylacetate. These values are in good agreement with previous studies for polyester dyeing [22, 24].

3.7.4. Enthalpy and Entropy of activation

The enthalpy and entropy of activation were calculated from the equations 7-12 respectively; by the theory of absolute rates of dyeing of Eyring equations were used. [27-32].

$$D = \lambda^2 \cdot e \cdot \frac{kT}{h} \cdot e^{-\Delta G^*/RT} \quad (7)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (8)$$

$$\Delta H^* = E_D - RT \quad (9)$$

$$D^* = \lambda^2 \cdot \frac{kT}{h} \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \quad (10)$$

$$D = D_0 \cdot e^{-E_D/RT} \quad (11)$$

$$D_0 = \lambda^2 \cdot e \cdot \frac{kT}{h} \cdot e^{\Delta S^*/R} \quad (12)$$

After simplification and deduction of the aforementioned equations we have reached to the equation 13 for calculating the entropy of activation.

$$\Delta S^* = R [\ln D_0 + \ln \lambda^2 \cdot \frac{kT}{h} - 1] \quad (13)$$

where ΔH^* is enthalpy of activation, ΔS^* is entropy of activation, E_D is the activation energy of the diffusion, T is the absolute temperature; R is the constant of ideal gases, h is Planck constant, k is Boltzmann constant, λ is the distance between two consecutive positions of the molecule diffused in the reaction coordinate (10 \AA). D is the apparent diffusion coefficient at $95 \text{ }^\circ\text{C}$ and D_0 is the slope of the line which was obtained from the linear adjustment of equation 7.

The values of D_0 for dyed PET samples with coumarin/n-butylacetate and o-vanillin/n-butylacetate were 1.978 and $3.544 \text{ Kcal}\cdot\text{mol}^{-1}$ respectively.

Table 9 shows the values of entropy and enthalpy of activation calculated from the theory of absolute rates of dyeing and diffusion of the activated state of the dye molecule with the aforementioned equations.

Table 9. Entropy and enthalpy and of activation for polyester samples dyed with C.I. Disperse Blue 56, coumarin or o-vanillin and n-butylacetate at 95°C

Activated state	polyester dyed with auxiliary products in microemulsion systems	ΔS^* (Kcal·mol ⁻¹ K ⁻¹)	ΔH^* (Kcal·mol ⁻¹)
		T=95 °C	T=95 °C
C.I. Disperse Blue 56 (0.333 g/L)	polyester dyed in microemulsion: coumarin/n-butylacetate/water (0.666/16.666g/L)	0.01305	3.19
	polyester dyed in microemulsion: o-vanillin/n-butylacetate/water (0.666/16.666g/L)	0.01422	6.30

As shown, the enthalpy of activation obtained for polyester dyed with disperse dye C.I. Disperse Blue 56 with o-vanillin/n-butylacetate microemulsion at 95 °C was significantly higher than polyester dyed with coumarin/n-butylacetate microemulsion. The higher value for the enthalpy of activation indicates a greater energy releases in the dyeing process for absorbing the dyestuff by the polyester [32]. Higher value of the entropy of activation obtained for the polyester dyed with o-vanillin produces higher changes in segmental mobility within the microstructure of the fiber that would produce higher facilities of randomness than coumarin so facility the diffusion inside the fiber. Both microemulsion systems can be associated with the dye for transport it to the fiber surface. However o-vanillin/n-butylacetate is more hydrophilic, therefore dye transportation to the fiber is made easier than coumarin/n-butylacetate. Such as explained before, deposition of dye molecules in the fiber surface is made dye molecule

after breakup. The microemulsion particle in the system of o-vanillin/n-butylacetate, is more realized for their diffusion into the fiber, as indicated for the higher entropy value.

From the thermodynamic results it was found that, the reaction was in a favor of the products.

According to the enthalpy, entropy of activation, it was determined that the absorption process of polyester samples dyed with C.I. Disperse Blue 56 is an endothermic process. Therefore, dye absorption increases with increasing temperatures [33; 34, 35].

This study reported that, before moving to the equilibrium state, the dyeing processes may obtain heat from the system, therefore values of enthalpy and entropy that obtained in the thermodynamic activated state could be larger than the equilibrium state [11, 22].

In this sense, it has to be noted that it is necessary to have the dye molecule in the activated state to overcome the energy barrier to diffuse into the fiber.

3.8. Ironing fastness

To analyze the color fastness to ironing, UNE-EN ISO 105-X 11 standard was applied at three temperatures: 110, 150 and 200 °C. Values of the degradation and discharge ironing fastness of the dyed polyester samples are shown in the Tables 10 and 11.

Table 10. Values of degradation ironing fastness of the polyester samples dyed with Disperse Blue 56 in the presence of o-vanillin/co-solvent or coumarin/co-solvent at 4 studied temperatures after 120 minutes.

PET fabric dyed 120 minutes	Degradation values of ironing fastness (Gray Scale)					
	Auxiliary : Coumarin			Auxiliary : O-vanillin		
Temperature	110 °C	150°C	200°C	110 °C	150°C	200°C
C.I. Disperse Blue 56 at 65 °C	4	3-4	2	4-5	4	2
C.I. Disperse Blue 56 at 75 °C	4-5	4-5	3	4	4	2-3
C.I. Disperse Blue 56 at 83 °C	4-5	4	3	4	4	4-5
C.I. Disperse Blue 56 at 95 °C	4-5	4-5	4	4-5	4	4-5

Both auxiliaries and the co-solvent used did not modify the degradation ironing fastness of the dyed samples; except at 200 °C of ironing values which are around 2-3. Polyester samples dyed with coumarin/co-solvent showed slightly better values of degradation ironing fastness properties than samples dyed with o-vanillin/co-solvent.

Table11. Values of discharge ironing fastness of the polyester samples dyed with Disperse Blue 56 in the presence of o-vanillin/co-solvent or coumarin/co-solvent at 4 studied temperatures after 120 minutes (polyester discharge).

PET fabric dyed after 120 minutes	Discharge ironing fastness (Gray Scale)					
	Auxiliary : Coumarin			Auxiliary : O-vanillin		
Temperature	110 °C	150°C	200°C	110 °C	150°C	200°C
C.I. Disperse Blue 56 at 65 °C	4-5	4-5	3	5	4-5	3-4
C.I. Disperse Blue 56 at 75 °C	4-5	5	3-4	5	5	3
C.I. Disperse Blue 56 at 83 °C	4-5	5	3	4-5	5	3
C.I. Disperse Blue 56 at 95 °C	5	5	3	5	5	3

In terms of discharge ironing fastness, there were no significant changes on the properties of dyed samples, and both auxiliaries have almost similar values, however at 200 °C of ironing values are around 3. In general polyester samples dyed with o-vanillin/co-solvent indicated slightly better values of discharge ironing fastness.

3.9 Color fastness to washing

To determine color fastness values to washing of the dyed samples, polyester fabrics were washed based on the UNE-EN ISO 105-C06 standard. Values of color fastness to washing are shown in the Table 12.

Table 12. Values of color fastness to washing of polyester samples dyed with Disperse Blue 56 in the presence of o-vanillin/co-solvent or coumarin/co-solvent at 4 studied temperatures after 120 minutes.

PET fabrics dyed after 120 minutes	Auxiliary : Coumarin			Auxiliary : o-vanillin		
	Gray Scale for evaluating change in color	PET (Gray scale for evaluating staining)	Cotton (Gray scale for evaluating staining)	Gray Scale for evaluating change in color	PET (Gray scale for evaluating staining)	Cotton (Gray scale for evaluating staining)
C.I. Disperse Blue 56 at 65 °C	3	3	2-3	2-3	3	2-3
C.I. Disperse Blue 56 at 75 °C	4	3-4	2-3	4-5	3	3
C.I. Disperse Blue 56 at 83 °C	3	4	3-4	4-5	4	3
C.I. Disperse Blue 56 at 95 °C	4	4-5	4	4	4-5	3-4

Either use of coumarin/co-solvent or o-vanillin/co-solvent did not change the washing fastness properties of the dyed samples significantly, as values are almost in good agreement with previous studies [2; 3, 36]. However values obtained for polyester dyed with o-vanillin/co-solvent were slightly better than the samples dyed with coumarin/co-solvent.

4. Conclusions

The purpose of this paper was to study the dyeing process of a polyester fabric with low molecular weight disperse dye (C.I. Disperse Blue 56), included in a microemulsioned system with n-butylacetate as a co-solvent (low environmental impact) and testing two biobased auxiliaries, o-vanillin or coumarin, selected with different affinity for the medium aqueous of dispersion. The studied temperatures were below 100°C, so lower than the conventional dyeing process around 135°C that promotes saving of energy

during the dyeing process with auxiliaries in form of microemulsion particles including the hydrophobic molecules of disperse dye with low toxicity than conventional carriers. The particle size of the microemulsified system o-vanillin /n-butyl acetate and coumarin/n butylacetate were similar including the same dye molecule into the system.

From results of the rate of the absorption kinetic of free disperse dye molecule to the fiber by the transport of the particles for the o-vanillin/n-butylacetate system were higher than for coumarin/n-butyl acetate system. This behavior is explained for the more hydrophilic dyeing bath of o-vanillin than coumarin dyeing bath more hydrophobic. The facility of the deposition of the free dye molecule at the surface in function of the auxiliary used showing their kinetic different absorption behavior and the diffusion later into hydrophobic fiber.

This phenomenon of liberation of free disperse dye molecule was justified for the more instable particle including the auxiliary o-vanillin for its higher hydrophilicity than the particles including coumarin, In consequence at the surface of the fiber the kinetic of the free dye molecule for their diffusion inside the fiber was higher for the system o-vanillin /n-butylacetate .

The highest values of the rate constant of the isotherms absorption and the activation energies of the disperse dye at 65°C, 75°C, 83°C and 95°C for the microemulsion o-vanillin/n-butylacetate than coumarin/n-butylacetate indicates the higher absorption kinetic process and the higher diffusion coefficient values (at 95 °C highest exhaustion found) for o-vanillin. From the apparent activation energy at the range of temperatures studied it was found that the action of microemulsion of o-vanillin/n-butyl acetate during the absorption kinetic process was more influenced by the variation of the temperature than coumarin/n-butyl acetate

The activated enthalpy and activated entropy and was calculated by the theory of absolute rates of dyeing and diffusion in the activated state. Higher value for the enthalpy of activation indicates a greater energy releases in the dyeing process for absorbing the dyestuff and higher entropy of activation obtained for in presence o-vanillin/butyl acetate produces higher changes in segmental mobility within the microstructure of the fiber so justify the more efficiency of kinetic and diffusion inside the fiber than coumarin/n-butylacetate.

According to the first thermal transition observed on the DSC curves, it was found that, presence of the co-solvent changed the thermal characteristics of the dyed polyester samples compared to the dyed polyester sample without using auxiliaries.

The calculated enthalpy and entropy of activation showed that the absorption of the polyester samples dyed with C.I. Disperse Blue 56 was an endothermic process, as expected.

Based on color fastness to washing and ironing tests, it was observed that there were no significant changes on the fastness properties of the dyed samples, as values were in good agreement with previous studies.

Furthermore, comparing this new process with a conventional one at 135 °C, it was found that similar results in terms of color strength were obtained with the 95 °C process presented in this paper, while avoiding high temperature, energy and cost of the dyeing process.

5. References

1. Carrión -Fité, FJ. Spanish patent number: P201630513. Priority date: 22/04/2016.
2. Carrión-Fité, FJ.; Radei, S. Development auxiliaries for dyeing polyester at low temperatures. IOP Conf. Ser. Mater. Sci. Eng. 2017; 254, 082006. doi:10.1088/1757-899X/254/8/082006.
3. Radei, S., Carrión-Fité, FJ.; Ardanuy M., Canal, J.M. Kinetics of Low Temperature Polyester Dyeing with High Molecular Weight Disperse Dyes by Solvent Microemulsion and AgroSourced Auxiliaries. *Polymers* 2018; 10,:2, doi:10.3390/polym10020200.
4. Gao A, Hu L, Zhang H, FU D, Hou A, Xie K. Silicone nanomicelle dyeing using the nanoemulsion containing highly dispersed dyes for polyester fabrics *Journal of Cleaner Production* 2018; 200, 48-53.
5. Parvinezade Gashti M, Moradian S. Effect of nanoclay type on dyeability of polyethylene terephthalate/clay nanocomposites *Journal of Applied Polymer Science* 2012; 125 (5), 4109-4120.
6. Parvinezade Gashti M, Ebrahimi I, Pousti M, New insights into corona discharge surface ionization of polyethylene terephthalate via a combined computational and experimental assessment *Current Applied Physics* 15 (2015) 1075-1083.
7. Pasquet V, Perwuelz A, Behary N, Isaad J. Vanillin, a potential carrier for low temperature dyeing of polyester fabrics. *Journal of Cleaner Production* 2013; 43: 20-26,doi:10.1016/j.jclepro.2012.12.032.
8. World Health Organization. Concise International Chemical assessment Document 64, n-butylacetate. 2005; Geneva Switzerland.
9. Shyam DP, Saptarshi M, Ravindra V A. Investigation of Thermodynamic-Kinetics of Polyester Dyeing with Liquid Disperse Dye. *Trends Textile Eng Fashion Technol* 2018; 4(2). TTEFT.000581.2018. DOI: 10.31031/TTEFT.2018.04.000581.
10. Shen JJ, Yang Y. Kinetics and Thermodynamics Studies of Prodigiosin Dyeing on Polyester. *Trans Tech Publications, Switzerland* 2013; 779–780: 156–60 , doi:10.4028/www.scientific.net/AMR.779-780.156.
11. Ghaharpour M, Rashidi A, Tayebi H. Adsorption Behavior of Disperse Orange 30

- on Polyester Fabric. *World Appl. Sci. J* 2011;14:1291-1295.
12. Patterson D. and Sheldon RP. The dyeing of polyester fibers with disperse dyes Mechanism and kinetics of the process for purified dyes. *Trans Faraday. Soc.* 1959; 55 1254.
 13. Peters L and Lister, GH. *Trans Faraday Soc.* 1954; 16, 24.
 14. Eyring H, Gershinowitz H, Sun CE. The absolute rate of homogeneous atomic reactions. *J Chem Phys* 1935;3:786–96.
 15. Swinehart DF. The Beer-Lambert Law. University of Oregon Eugene. 1962; 39:333-335.
 16. Hansen, C. Hansen Solubility Parameters, 2nd edition. CRC Press Inc.: Boca Raton, FL, USA; 2000, pp. 252-478.
 17. Burkinshaw, SM. *Chemical Principles of Synthetic Fibre Dyeing*. Blackie Academica & Professionnal, London; 1995.pp. 2-15.
 18. Van Ness, JH. "Vanillin".*Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edition. New York: John Wiley & Sons; 1983, pp.704–717.
 19. Venugopala KN, Rashmi V, Odhav B. Review on Natural Coumarin Lead Compounds for Their Pharmacological Activity. *BioMed Research International*. 2013:1-14. DOI:10.1155/2013/963248.
 20. Carrión-Fité FJ. Dyeing Polyester at Low Temperature: Kinetics of Dyeing with Disperse Dyes. *Text. Res. J.* 1995; 65, 362–367.
 21. Cegarra J., Puente P. and Carrión, FJ. Empirical Equations of Dyeing Kinetics. *Text. Res. J.*, 1982; 193-197.
 22. Georgiadou KL, Tsatsaroni EG, Eleftheriadis IC, Kehayoglou AH. Disperse dyeing of polyester fibers: Kinetic and equilibrium study. *J Appl Polym Sci* 2002; 83: 2785–2790. doi: 10.1002/app.10254.
 23. Arrhenius S. Uber die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Sauren (On the reaction rate in the inversion of cane sugar by acids). *Z Phys Chem* 1967; 1889; 4:226–48.
 24. Kim TK, Son YA, Lim YJ. Thermodynamic parameters of disperse dyeing on

- several polyester fibers having different molecular structures. *Dye Pigment* 2005; 67: 229–234, doi:10.1016/j.dyepig.2004.12.005.
25. Crank J. *The mathematics of diffusion* clarendon press oxford; 1975, pp.38-47.
26. Crank J. and Park G.S. *Diffusion in Polymers*. 1st Edition, Academic Press, London and New York; 1968.
27. Low PS, Bada JL, Somero GN. Temperature adaptation of enzymes: roles of the free energy, the enthalpy, and the entropy of activation. *Proc Natl Acad Sci U S A* 1973; 70: 430–432.
28. Eyring H. The activated complex in chemical reactions. *J. Chem. Phys* 1935; 3:107-115.
29. Glasstone, S. *Physical chemistry D*. Van Nostrand company Inc.; USA; 1940, pp.205-235.
30. Barrer RM, Barrie JA, and Slater JJ. *Polimer Scien.*; 1958, 27,177.
31. Vickerstaff T. *The Physical Chemistry of Dyeing*; 2nd edition. (Oliver and Boyd, London).
32. Atkins P, Paula J. *Elements of physical chemistry*, 5th edition. Oxford University Press, 2009; pp.40-214.
33. Elsis AA, Emam AA, Gomaa SH, Ahmed HM. Enhancement of dyeing Technology of Polyester fabric with disperse red 167 using ZnO Nano Powder Specialty *Journal of Chemistry* 2016; 1(1): 6-18. Available online at <http://www.sciarena.com>.
34. Otutu, JO, Ameuru US. Thermodynamic Sorption Parameters and Kinetics of Dyeing Disazo Dyes Derived from 4-aminobenzoic acid and 4-amino-3-nitrotoluene on Polyester Fibre and Polyamide Fibre. *Br. J. Appl. Sci. Technol* 2014; 4(20): 2955–2969.
35. Hou X, Yang R, Xu H, Yang Y., 2012. Adsorption kinetic and thermodynamic studies of silk dyed with sodium copper chlorophyllin. *Ind Eng Chem Res* 2012; 51:8341–8347.
36. Harifi T and Montazer M. Free carrier dyeing of polyester fabric using nano TiO₂. *Dyes Pigment* 2013; 97, 440–445.