ECOFRIENDLY TECHNOLOGY FOR REACTIVE DYEING OF CATIONIZED FABRICS: PROTIC IONIC LIQUIDS AS INNOVATIVE MEDIA

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Because of the limitations of traditional dyeing technologies, large amounts of water and chemical additives are used in the dyeing processes, resulting in enormous quantities of polluted wastewater, which has a huge health and environmental potential impact. In the last few years, the interest in researching alternative techniques/materials for the textile industry to reduce the consumption of water used to improve dyeing quality, has considerably increased. Continuing previous research, in this paper, we present a non-aqueous dyeing procedure, testing different types of fabrics with a polyfunctional reactive dye and protic ionic liquids (PILs) as reaction environment, and with cationization pretreatment of the tested fibers. To analyze the effectiveness of the proposed procedure, currently established dyeing quality parameters, such as color absorption and wash fastness of the dyed multifiber fabrics, have been measured and analysed. The obtained dyeing results should be explained by the affinity of cationized multifibers to the reactive dye, as well as by the efficiency of the mechanisms of dye diffusion and chemical bonding on the tested fabrics in protic ionic liquid environment. This new proposed "universal dye" for all kinds of fibers in PIL environment was analyzed under different operational dyeing conditions. The obtained results were satisfying when compared with standard dyeing quality parameters reported in earlier published literature, thus opening opportunities for innovation and optimization.

Keywords: textile dyeing, reactive dye, cationization, multifiber fabrics, protic ionic liquids

INTRODUCTION

The textile industry has been frequently criticized for its negligence towards ecosystems, being responsible for 10% of global carbon emissions into the atmosphere, the second-largest consumer of water in its processes and its business model being far from the concept of circular economy. The textile industry continues in the XXI century using techniques and procedures that raised doubts in terms of sustainability and job security. This contradicts the general concern and the initiatives of social responsibility of the wide world companies, partly because of the massive relocation around the globe of the textile sector in developing countries and the poor surveillance of production processes. The increasing demand in the textile industry is due to a culture of mass consumption and at low prices. This fact has generated global environmental problems, mainly because of the technology associated with dyeing of fabrics and the final disposal of clothes at their end-of-use. Moreover, the final disposal of clothes by burying them in landfills is a poorly solved problem, increasing in volume year after year (in USA, approximately 85% of urban waste in landfills consists of textile materials), and generating a leaching mass of toxic products, slowly incorporating into water flows and natural biota.

Textile dyeing is based on ancient techniques that began thousands of years ago, using natural dyes extracted from plants, animals, and different types of minerals. Nowadays, industrial dyeing processes include synthetic dyes and a wide spectrum of chemical additives for application of color to textile fibers.¹⁻⁸ The procedure is carried out in aqueous media, constantly at high temperatures. Large

amounts of water are used by the textile industry, up to 200 liters to produce 1 kg of textiles, depending on the type of fiber and dye used, only 20% of this total being actually associated to the dyeing process,⁹⁻¹³ thus producing large quantities of wastewater and generating additional costs, given the need for chemical and biological treatment before discharge of the process water into the environment and severe environmental impact if this treatment is not carried out. Finally, the global process cost is huge in environmental and job security/economical terms, from the first step of the production chain to the final disposal of the product after its life cycle.¹⁴⁻¹⁷

The textile fiber can be natural, synthetic, regenerated or modified. Its nature and chemical structure characteristics, as well as the used chemical additives, technology and equipment, the quality of the dyeing solvent (usually water), economic considerations, among others, define the number of steps of dyeing¹⁸⁻²⁰ and influence its final quality. To guarantee uniformity in color and colorfastness to agents that would cause fading, as well as to reduce disposal of unfixed substances, the fiber and chemicals used to dye must present high affinity and selectivity. Different studies have shown that one billion kilograms of dyes are produced in the world every year and, as a consequence, the amount of dyes released into the environment reaches 1-2 million kilograms, considering unfixed dye molecules during the textile processes.²¹⁻²³

In recent years, the need to reorient the dyeing process towards cleaner methodologies that minimize the use of chemical additives and water has been pointed out, seeking alternative solutions without compromising the final quality of the dyed fabrics. Currently, the textile industry presents its center of gravity in developing countries, with population with a low income status, with training substantially below the average for the manufacturing industry²⁴⁻²⁶ (Fig. 1). The Brazilian textile and clothing sector stands out on the world market, mainly due to the size of its textile park, which is the fifth largest global textile industry. As an emerging industrial sector, its development is recent, progressive and mainly linked to previously established industrial areas with nearby sea export points (mainly South and Southeast regions in Brazil). The so-called *Região do Pólo Têxtil* (RPT) (Textile Pole Region, in São Paulo) is the largest pole of the textile and clothing industry in Brazil, responsible for 85% of the national production of artificial and synthetic fabrics and, for this reason, considered the largest textile pole of artificial/synthetic fibers in Latin America (Fig. 2).



Figure 1: Worldwide distribution of Human Development Index (HDI) for the highest textile exporting countries and 3D projection of gross domestic product (10^{12} US\$, International Monetary Fund data, 2018), global share as textile industry producer (%) and HDI



Figure 2: Human Development Index (HDI) distribution in Brazil for the highest textile producing states and 3D projection of gross domestic product (10^{12} US\$, International Monetary Fund data, 2017), global share as textile industry producer (%) and HDI

The textile industry is always the sector of the future because it seems that it will be updated later, and eternally delocalized to poorer countries, and it continues to show enormous potential for optimization, but scarce steps are taken in the direction of significant technological improvement. All the processes within the textile industry should be reevaluated constantly to reduce the environmental impact and social costs.²⁷⁻²⁸ The complexity of the conventional dyeing process is one of the biggest concerns, because it includes the consumption of water (with expensive chemical and biological remediation processes), pollutant dyes and the difficulty of reusing wastewater. Technically, these environmental issues can be analyzed and, perhaps, solved with biodegradable, less toxic products and new materials that are being developed.²⁹⁻³⁴

Almost all natural dyes are unable of, by themselves, permanently coloring fabrics, attending to actual quality requirements, therefore, most of the used dyes in the textile industry are synthetic. Due to the variety of fibers usually processed in textile industries, several different dyes are manufactured today, and the number is rapidly increasing – the Colour Index International lists 27,000 individual products under 13,000 Colour Index generic names³⁵ – which leads to environmental problems, mainly related to water contamination by unfixed dye, dispersion of many other auxiliary chemicals related and deep ignorance of the decomposition chemistry paths of these compounds, their future interaction with the natural environment and the unwished-for alteration of the microbiota. The volatile chemicals used pose particular problems, because they evaporate into the air or are absorbed into foods or through skin. Some chemicals are carcinogenic or may trigger allergic reactions in some people.^{15,36-37}

The rate of color fixation into the fabrics varies considerably among the different dye classes and according to the chemical auxiliaries contained in the dyebath, generating the need for specific treatments for each type of produced wastewater. The potential use of a reactive dye as "universal dye" for all kinds of fibers can represent a significant innovation in the textile chemistry, reducing the complexity of both the dyeing process and the wastewater treatment.³⁸⁻⁴¹

Reactive dyes chemically react with the fibers by formation of covalent bonds between dyes and fiber, producing a hydroxyl and an oxygen linkage, the chlorine combining with the hydroxyl to form a strong ether linkage. The reactivity of these dyes is due to the chlorine atoms attached to the haloheterocycle ring. When two chlorine atoms are present on the dye molecules, one of the chlorine atoms is so reactive that it reacts with cellulose even at room temperature in the presence of an alkali (cold brand reactive dyes). When only one chlorine atom is present in the dyestuff molecule, the reactivity of the dye decreases considerably, and the dyeing has to be carried out at higher temperature (65-80 °C) (hot brand reactive dyes).

Reactive dyes first appeared commercially in 1956, after their invention by Rattee and Stephens at the Imperial Chemical Industries Dyestuffs Division. Reactive dyes are the most important class of

Due to their brilliant shades, excellent wet fastness of dyeing and simple dyeing operations,⁴² they have been increasingly well accepted by the public and the industry. Despite their good fastness properties, reactive dyes have a lower utilization degree, compared to other types of dyestuffs, mainly since the functional reactive group also bonds to water, producing considerable dye hydrolysis. The dyeing process is essentially an isothermal homogeneous distribution process of the dye through two different phases (liquid dye bath and solid fabric structure), a physico-chemical equilibrium being reached. Most of the dyes in the dyeing bath are dispersed as a real molecular solution (mainly in additivated aqueous media), ionized in any degree or ionic micelles. A concentration gradient is produced when the solid fabric is introduced into the dye media, a diffuse transference of dye being produced near the surface of the fabric. All textile fibers, when immersed in water or aqueous solution, acquire an electrical potential, producing an extremely close electrical double layer of non-solvated anions and solvated cations that dyes must cross to reach the fabric surface. After the dye molecules approach the fabric surface, this first layer of solid fibers takes them up fast, decreasing dye concentration at the vicinity of the solid substrate. Finally, after this first stage of superficial absorption, deep diffusion into the fabric structure occurs, a strong one-way covalent chemical bond fixation of the reactive dye being produced.

The structure of a reactive dye contains five types of functional molecular structures: chromophore groups, solubilizing groups, bridging groups, reactive groups and leaving groups; each of them influences the dyeing and its fastness properties.⁴³ The chromophore structure is responsible for the color of the dye. The solubilizing group is responsible for dye's solubility in the operation medium, level of migration and resistance to washing. To connect the chromophore to the reactive group, there is one or more bridging groups. The reactive group is responsible for the chemical interaction with the fiber and, at last, the chemical bonds to fix the dye into the fabric. Reactive dyes are capable of making a covalent bond with hydroxyl groups of the cellulosic fibers, with amino, hydroxyl and thiol groups of the protein fibers and also with amino groups of the polyamides.

Before dyeing, it is commonly necessary to modify the fiber surface structure, using both chemical and physical techniques of pretreatment.⁴⁴⁻⁵¹ The procedure of cationization is a process used to create a film over a textile substrate to enable it to receive the dyeing process afterward,⁵²⁻⁵⁵ and can be used to avoid or, at least, minimize the usage of chemical additives in the dye bath. The cationic agent modifies the chemical structure of a specific area of the fabric producing active fields. More specifically, cationization is used to change the surface charge of textile fibers, introducing cationic sites into them, because they usually show inert anionic charges in solutions.⁵⁴ So, this technique is carried out to improve the affinity toward anionic dyes in textile processing. In addition to increasing the final quality of the dyeing, the presence of cationized groups in the fabric also imparts antimicrobial properties.⁵⁶⁻⁵⁷ Likewise any other chemical additive in the dyeing process, cationizers facilitate the fixation stage, but also increase the chemical load of the fabrics and potential transfer to the environment during its elaboration and during/after its useful life. Aspects of physical, chemical, human safety, environmental safety, and safe handling, storage and disposal of cationizers have been examined and reviewed; in general terms, they are only slightly toxic to freshwater organisms and have low levels of oral and dermal toxicity for humans; are not skin or eye sensitizers, have very low vapour pressure, and inhalation risks are not expected.⁵⁸⁻⁶⁰ Considering all the factors in relation to the dyeing process, it should be asseverated that the role played by the liquid medium in which the fabric impregnation occurs is likely to produce the greatest impact on global optimization due to its role in terms of diffusion, electric nature, and solvation capability. There are many factors affecting the dyefiber affinity, one of them being the fiber-solvent interaction. The fiber ability of solvent absorption, known as its swelling ability, affects the dye penetration into the fiber.

Ionic liquids (ILs) are new solvents with several desirable characteristics that have been used as alternative solvents in many industrial applications in the last few decades.⁶¹⁻⁶⁶ Many recent works have shown the potential of ILs to assist in textile processes, as regenerating⁶⁷⁻⁶⁸ or dissolution⁶⁹⁻⁷¹ agents of cellulosic fibers, of help in the felting resistance of wools,⁷²⁻⁷³ in the degumming of silk,⁷⁴ to impart hydrophilicity, smooth surface and brightness through alkaline hydrolysis of polyester;⁷⁵ to produce a modification in the surface and internal structure of wool fibers, making the dye molecules easily adsorbed and directly diffused into the fabric;⁷⁶⁻⁷⁷ to enhance the dyeability of wool and silk fabrics with acid and reactive dyes at low temperatures;⁷⁸⁻⁷⁹ for the pretreatment of ramie fibre to improve its dyeability by C.I. Reactive Yellow 4;⁸⁰ for replacing traditional inorganic salt in dyeing

bath;^{41,81-82} and as the only solvent in the dyebath instead of water.⁸³⁻⁸⁶ Ionic liquids can be divided into two large groups: aprotic ionic liquids (AILs) and protic ionic liquids (PILs).⁸⁷ The ionic liquids studied in this work belong to the second group, PILs, which include substances potentially biodegradable in soil and water,⁸⁸⁻⁹⁰ with lower toxicological profile and higher IC₅₀ values (concentration required for achieving 50% inhibition of the cell culture), when compared to imidazolium/piridinium derived ionic liquids assessed for HepG2 and HaCat human cells,⁹¹⁻⁹² as well as lower production costs. They commonly enclose polysubstituted amines as cations and organic acids as anions, with different numbers of carbon atoms and without complex structures or potentially hazardous molecular groups, using steric hindrance of short aliphatic chains as a mechanism of "atom economy" and low ionic net energy. Our research group analyzed in the last few years various aspects of potential applications of a wide range of protic ionic liquids.^{86,92-107}

The aim of this work is to analyze the performance of a newly proposed method for dyeing diacetate, cotton, polyamide, acrylic and wool fibers, avoiding the use of several chemical additives and of large amounts of water. This process involves a cationization pretreatment and non-aqueous dyeing using protic ionic liquids as the only solvent and a polyfunctional reactive dye, Drimaren Yellow CL – 2R (Clariant), which contains a combination of triazines and vinyl sulfone groups, with fixation and solubilization functions, respectively. This dye has been chosen due to its higher tolerance to temperature deviations and fastness (better quality) in the dyeing process. To analyze their effectiveness as dyeing solvents, a range of PILs with homologous chemical structure (rising number of methylene molecular group in the aliphatic chain in the anion) were analysed: 2-hydroxy diethylammoniumacetate (2-HDEAA), 2-hydroxy diethylammonium propionate (2-HDEAPr), 2-hydroxy diethylammonium butanoate (2-HDEAB) and 2-hydroxy diethylammonium pentanoate (2-HDEAP). The final dyeing properties of the dyed multifiber fabrics, as color strength, colorfastness to rubbing and colorfastness to perspiration, are also reported in this work.

EXPERIMENTAL

The complete synthesis protocol, spectrometric analysis and thermodynamic characterization of the used protic ionic liquids: 2-hydroxy diethylammonium acetate (2-HDEAA), 2-hydroxy diethylammonium propionate (2-HDEAPr) and 2-hydroxy diethylammonium pentanoate (2-HDEAP), have been previously reported by the authors.^{86,97,104,106} Figure 3 shows the chemical structure for each PIL.

For 2-hydroxy diethylammonium butanoate (2-HDEAB), after synthesis following the same protocol, the thermodynamic and spectrometry analyses were carried out in order to establish their ionic salt structure and to ensure the purity of the product before experimental measurements and dyeing analysis in our lab (Figs. 4-6).

Spectrometric characterization

All of the NMR experiments were performed at 298.15 K in a Bruker spectrometer operating at 750 MHz proton frequency. The spectra were processed with Mestre-C software. Sample preparation required only the transfer to a 5 mm NMR tube. An external reference standard capillary, containing deuterated 3-(trimethylsilyl)propionic acid-d4 (TSP) [0.1 M in dimethyl sulfoxide (DMSO)], was introduced coaxially into the tube. The TSP signal at approximately 0 ppm was used to determine absolute concentrations in the one-dimensional (1D) proton spectrum, and the DMSO was used for deuterium lock. The integral of the 1 H NMR signal of TSP in the capillary was calibrated with respect to a sample of 0.2 M sucrose dissolved in D_2O prepared in a 5 mm NMR tube. The anomeric glucose proton appearing at 5.2 ppm was chosen for the calibration.



Figure 3: Chemical structure of protic ionic liquids (from right to left): 2-hydroxy diethylammonium acetate (2-HDEAA), 2-hydroxy diethylammonium propionate (2-HDEAPr), 2-hydroxy diethylammonium butanoate (2-HDEAB) and 2-hydroxy diethylammonium pentanoate (2-HDEAP)





Quantitative $1D^1$ H NMR spectra were acquired with a 33° pulse and a conveniently long interscan relaxation time (d₁ 10 s). These conditions were used to ensure the exactness of the signal integration. The 1H NMR spectrum (Fig. 4) shows two multiplets, at δ 3.25 and δ 3.87, referring to methylene hydrogens. The sign at δ 2.16 as a triplet was assigned to the alpha methylene hydrogens of the carboxylate, and δ 1.56 (sextet) to the beta hydrogens of the carboxylate. The triplet at δ 0.90 refers to methyl hydrogens.

2D heteronuclear single-quantum coherence (HSQC) and 2D heteronuclear multiple-bond quantum coherence (HMBC) NMR spectra were acquired using standard methodologies. These 2D experiments (Figs. 5-6) provided H-H and H-C through-bond correlations that assisted the NMR signal assignment and confirmed the synthesized structure.

Thermodynamic measurements

Densities and ultrasonic velocities were measured using a DSA-5000 digital vibrating tube densimeter (Anton Paar, Austria). The apparent viscosities of the IL samples were analyzed using a Visco Elite L Rheometer (Fungilab, Spain) at different temperatures. The refractive indexes of the ILs were analyzed by an automatic digital RX-5000 refractometer (Atago, Japan). The surface tensions were measured using a Kruss K-9 tensiometer, which employs the Wilhelmy plate principle. Ion conductivity was measured by a Jenway Model 4150 Conductivity/TDS Meter, with resolution of 0.01 S to 1 mS and accuracy of $\pm 0.5\%$ at the range temperature.

Cationization

The cationic agent used in this work was (S)-(-)-(3-Chloro-2-hydroxypropyl) trimethylammonium chloride, CHPTAC (CAS Number 3327-22-8), from Coratex® (see chemical structure in Fig. 7). In this procedure, reagent-grade NaOH crystals, purchased from Merck, with richness higher than 99.0 mol%, were also used to balance the pH of the solution with continuous mixing. The multifiber samples were thermostated for 15 minutes

with the cationizer, concentration of 5 wt% (multifiber fabric weight: cationizer weight), distilled water (1:10) and solid NaOH 1 wt% (multifiber fabric weight: NaOH weight) at 333.15 K.

Dyeing procedure

The dyeing process was carried out with multifiber fabrics MFF#42, according to ISO TC 274E-3 (diacetate, cotton, polyamide "Nylon 6.6", polyester "Dacron 54", acrylic "Orlon 75" and wool), and a polyfunctional reactive dye Drimaren Yellow CL - 2R (Clariant). Its chemical structure is shown in Figure 8. The dye concentration was 1 wt% (multifiber fabric weight: dye weight); the R:B ratio (multifiber fabric weight versus bath weight) was fixed to 1:10, and the dyeing temperature was set to 333.15 K, according to the common practice of fabric dyeing in industrial processes.

Experimental dyeing tests were developed using a Kimak[®] device, model AT1-SW. The reactive dye, protic ionic liquid and fabric were weighed in the quantities indicated before (METTLER AT-200 Analytical Balance, accuracy better than $\pm 10^{-4}$ g), placed in dyeing vats and introduced into the Kimak[®]. The equipment started, rising the temperature from 298 K to 353 K in 10 minutes (0.5 K/min), the dyeing temperature was kept stable at 353 K for 40 minutes (Fig. 9) in order to reach the highest coloristic intensity values.

Each fabric was dyed using a specific PIL, and then the bath was cooled for 5 minutes. The excess of PIL from the fabric was removed with foulard equipment, subsequently washed with water until no colored water removal was obtained. After the complete removal of PIL and possible unfixed dye from the fabric, all the samples were dried at ambient temperature under natural convection and at a constant humidity/temperature (70% humidity and 298.15 K at atmospheric condition) in a laboratory incubator.



Figure 7: Chemical structure of cationizer (S)-(–)-(3-Chloro-2-hydroxypropyl) trimethylammonium chloride

Figure 8: Chemical structure of Drimaren Yellow CL-2R (Clariant) dye



Figure 9: Process curve for dyeing of multifiber fabrics with reactive dye in protic ionic liquids

Color measurement and other quality parameters

Reflectance measurements are normally applied to determine the color strength of dyes adsorbed in a substrate. Reflectance is the ratio of reflected light and incident light (electromagnetic radiation flow) on a specific surface. Thus, all the dyed fabric samples were directly monitored for the wavelength of minimum reflectance, determined from the recorded reflectance spectra in the wavelength range from 400 to 700 nm (visible spectrum). The color strength of the dyed fabric samples was analyzed by a DATACOLOR[™] 550 spectrophotometer.

Based on the readings of reflectance for the samples at 450 nm (maximum absorption), the values of K/S

were calculated by using the extensively reported expression of Kubelka–Munk. According to the open literature, there is a well-established linear dependence of K/S on the color of a solid surface:¹⁰⁸

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$
(2)

where R is the measured reflectance, and K and S are the absorption and scattering coefficients of the dyed fabric, respectively.

In addition to the reflectance values, the spectrometer provides the tristimulus values (X, Y, Z), which were then transformed into the L*a*b* color space. The Commission Internationale de l'Eclairage (CIE) defined the L*a*b*(CIELAB) as a color space that describes all the colors visible to the human eye and was created to serve as a device-independent model to be used as a reference. For them, color can be determined and recognized as red or blue, for example, from specific L*, a* and b* coordinates. The parameter L* indicates lightness (100 = white, 0 = black), a* is the red/green coordinate (positive sign = red, negative sign = green), and b* is the yellow/blue coordinate (positive sign = yellow, negative sign = blue). In other words, they are defined by:

$$L = 116 (f_v - 16) \tag{3}$$

$$a = 500 (f_x - f_y)$$
(4)

$$b = 200 (f_y - f_z)$$
 (5)

where:

$$f_x = \begin{cases} \sqrt[5]{x_r} & x_r > \varepsilon \\ \frac{kx_r + 16}{116} & x_r \le \varepsilon \end{cases}$$

$$f_x = \begin{cases} \sqrt[5]{y_r} & y_r > \varepsilon \\ \sqrt[5]{y_r} & y_r > \varepsilon \end{cases}$$
(6)

$$f_y = \begin{cases} \frac{ky_r + 16}{116} & y_r \le \varepsilon \end{cases}$$

$$\begin{pmatrix} \sqrt[5]{Z_r} & Z_r > \varepsilon \end{pmatrix}$$

$$f_z = \begin{cases} \sqrt{2r} & 2r > \varepsilon \\ \frac{kz_r + 16}{116} & z_r \le \varepsilon \end{cases}$$
(8)

and

$$\begin{aligned} x_r &= \frac{x}{x_r} \end{aligned} \tag{9} \\ y_r &= \frac{y}{x_r} \end{aligned} \tag{10}$$

$$z_r = \frac{z}{z_r}$$
(11)

where X_r , Y_r and Z_r are reference coordinates (measured from a reference sample, dyed in conventional aqueous medium, without PIL), and the parameters ε and k are standard values fixed by CIE. Additionally, the color intensity was measured according to the Color Measurement Committee (CMC, UK), defined by a set of well-known equations from a large study of the acceptability of color differences in all regions of color space. All the types of fibers were analyzed.

Furthermore, the multifiber fabrics were subjected to dry and wet friction tests and analyses were performed as described in the Technical Norms of Brazilian Association (ABNT) and ISO standards methods. The ISO 105-X12 (ISO, 2019)¹⁰⁹ standard (Color fastness to rubbing) was used to evaluate the strength of the samples to color transfer. This standard is applied when evaluating the degree of color transfer from the dyed fabric to a control sample. The color transfer test evaluates the strength of the dyeing when in friction contact with other textile surfaces, both in dry and wet conditions, in which the dye can migrate to another fabric during a mechanical domestic washing process, for example. The ISO 105-E04 (ISO, 2014)¹¹⁰ standard was used for testing color fastness to perspiration. The evaluations of the control samples submitted to dry and wet friction contact tests were made according to the standard ISO-105-A03 (ISO, 2006)¹¹¹ (grey scale for assessing staining).

RESULTS AND DISCUSSION

Thermodynamics and spectrometric characterization

The application of ionic liquids in industrial processes requires information on their thermodynamic properties for equipment design, but also on their environmental impact and potential toxicity, considering the requirements of different regulatory agencies and new environmental policies. For instance, in order to comply with the provisions of REACH policy, adopted to guarantee the protection of environment and human health from the risks deriving from chemicals, as required by

any UE partner, companies must identify and manage the risks associated with the substances they manufacture and market in the UE, demonstrating how to use such substances safely. This regulation constitutes a milestone in the management of chemical substances and inspires policies and norms worldwide. The registration of new substances into the REACH database requires extensive physicochemical information, biodegradation data and toxicology effects, which at the moment are not available for ionic liquids.

The experimental measurements of density and ultrasonic velocity (Fig. 10), surface tension and refractive index (Fig. 11), kinematic and dynamic viscosity and ionic conductivities (Fig. 12), as a function of temperature, provide us a preliminary thermodynamic characterization of the protic ionic liquid 2-HDEAB. As already discussed, the other protic ionic liquids have been previously studied, 97,104,106,108 and, for this reason, in the present work, we focus on the thermodynamic characterization of 2-HDEAB only. A comparison of experimental results with literature data $^{97,108,112-116}$ for pure compounds at T = 298.15 K and other relevant information can be found in Table 1.

Knowledge of these thermodynamic properties is also valuable for textile industries, by providing a wide database for predicting and tuning the performance of PILs as dyeing bath medium. In textile processes, it is necessary to maintain different physico-chemical properties of the dye bath around acceptable range values. The possibilities of adapting the dye bath by combining solvents are wide (different PILs as dye bath, new functional additives *etc.*), so knowledge of different physico-chemical characteristics becomes important. Increasing values of surface tension, density and viscosity in the dye bath media, for example, could result in a significant reduction of fabric wettability during the dyeing process and, consequently, in loss of final dyeing quality.



Figure 10: Curves of density (gcm⁻³), ultrasonic velocity (ms⁻¹), isentropic compressibility (TPa⁻¹) and isobaric expansibility (K⁻¹) for PIL 2-hydroxy diethylammonium butanoate (2-HDEAB) in the temperature range of 278.15–338.15 K



in the temperature range of 278.15–338.15 K

PIL	Molar mass $(M, gmol^{-1})$	Density (ρ, gcm^{-3})	Ultrasonic velocity (u, ms ⁻¹)	Conductivity** $(\sigma,\mu Scm^{-1})$	Refractive index (n_D)	Dynamic viscosity (µ, mPas ⁻¹)	Surface tension $(\gamma, \text{mNm}^{-1})$
2-HDEAA	165.19	$\begin{array}{r}1.167483^{108}\\1.1755^{112}\\1.1766^{113}\\1.1745^{114}\end{array}$	$1863.35^{108} \\ 1788.71^{113} \\ 1608^{115}$	1051.38	1.46485 1.431 ¹¹⁵	363.4	55.25
2-HDEAPr	179.22	1.134793 ¹⁰⁸	$\frac{1730.48^{108}}{2207.86^{116^*}}$	542.52	1.46696	448.9	43.00
2-HDEAB	193.25	1.099279	1639.12	234.60	1.46986	942.1	37.24
2-HDEAP	207.27	1.072811^{97}	1590.19^{97}	218.80^{97}	1.46854^{97}	803.2^{97}	34.09^{97}

Table 1 Experimental and literature data for pure PILs at 298.15 K and other relevant information*

*Interpolated values from experimental data; **Mili- or micro-, see Fig. 10

A frequently applied derived property for industrial compounds is the isobaric expansibility or thermal expansion coefficient (α), expressed as the temperature dependence of density. Thermal expansion coefficients are calculated by means of $(-\Delta\rho/\rho)$ as a function of temperature and assuming that α remains constant in any thermal range. In the case of pure chemicals, it can be computed by the expression:

$$a = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{p,x}$$

(12)

taking into account the temperature dependence of density. As expected, these values showed an inflection point (in terms of negative values), as observed for other protic ionic liquids^{86.97} at around 300-310 K (see inset in Fig. 10).

A global comparison with previously published values for the other PILs belonging to the functional sequence proves the high influence of the anion aliphatic residue, due to its longer structure if compared with the cation, introducing a stronger disturbance in terms of molecule/ion accommodation. This fact may be observed in terms of higher values of density, ultrasonic velocity, conductivity and surface tension, compared with the earlier data of those salts of lighter anion. As observed in Figure 10, a progressive diminution of density and ultrasonic velocity of 2-HDEAB occurs at higher temperatures. This tendency is clearly shown in terms of isentropic compressibility (rising trend with temperature) and isobaric expansibility (concave trend as observed in the functional family of heavy anion protic ionic liquids). Analogously, in Figure 11, the refractive index and surface tension acquire lower values for higher temperatures, showing progressive weakening of ion-ion interaction in the ionic liquid net by higher ion mobility. In Figure 12, the viscosity (dynamic and kinematic) and ionic conductivity of the PIL are depicted, and a strong effect can be observed at higher temperatures. This fact may be ascribed to the rising ions mobility at higher temperatures, too. The ionic conductivity values decrease when the anion's branch increases, so, the lowest values for 2-HDEAP and the highest for 2-HDEAA could be observed in this ionic series, and all of them show lower ionic conductivity than the lighter members of this PIL family.^{86,94,97} The influence of anion residue (butirate anion in this case), comparatively with earlier results of the authors, is relevant in terms of steric hindrance, due to its longer structure.^{94,97,99} This factor produces a higher disturbance in ion package due to its relatively long chain structure, while the bulk cation (2-hydroxi diethanolamine cation) develops lower steric hindrance influence. Ion's mobility and progressively higher kinetics make more and more difficult the ion-ion interaction, rising dispersive effects among covalent residual branches and then weaker structures in the liquid phase. For example, Figures 13 and 14 reinforce these facts. In Figure 13, it should be observed the progressively decreasing values of density as a function of linear chain length of the anion (from formiate until pentanoate anion), evolving two types of cations (2-hydroxi monoethanolamine and 2-hydroxi diethanolamine). This figure shows earlier published data of the authors (and others from the available literature, for comparison) at 298.15 K, exhibiting a decreasing evolution for the rising Z parameter (Z being the number of methylene groups in the anionic chain of this protic ionic liquid family).^{97,99,104,106,112-130} Clearly, these data follow an approximately linear tendency (indicated by a continuous line). A second line (dashed) shows the evolution of density versus Z for the PILs of monoethanolamine cation. Analysing these lines, a series of conclusions could be defined: firstly, two almost parallel lines are observed, highlighting the similar influence of the Z factor on the protic ionic liquid density, independent of the cation (mono or diethanolamine); secondly, the diminishing trend of the two data collections for rising Z indicates the steric hindrance of the anion as main factor of the decrease of density; and thirdly, the position of the new experimental data of 2-HDEAB at 298.15 K enclosed in this work fits in perfectly, in terms of tendency and absolute value, in the set of previous values, disregarding the data that clearly do not follow the global trend of the open literature, ^{115,117-118} as observed in Figure 13.

In Figure 14, a comparison of isobaric expansibility versus temperature of the functional series of protic ionic liquids with diethanolamine cation (from 2-HDEAA to 2-HDEAP) should be observed. A decreasing sequence of isobaric expansibility at each temperature may be remarked. As mentioned, the new isobaric expansibility data for 2-HDEAB are easily enclosed into the collection of previously measured data for the other ionic liquids,^{97,106} showing a slighter concave trend than for 2-HDEAP, in opposition to the convex trend of 2-HDEAPr (convex, almost constant value of isobaric expansibility versus temperature) and 2-HDEAA (convex).



Figure 13: Density comparison between experimental and literature data at 298.15 K for ethanolammonium (\bigcirc) and diethanolammonium (\blacktriangle) based protic ionic liquids; Z is the number of methylene groups in the anionic chain (from acetate ion (Z=1) to pentanoate (Z=4)), as expressed in the empirical formulae $^{-}(OOC - (CH_2)_z - H)$; (----) trend line for monoethanolamine cation in PIL, (...) trend line for diethanolamine cation in PIL



Figure 14: Thermal expansion coefficients for (\bigcirc) 2-HEAA, (\bigtriangledown) 2-HDEAPr, (\blacksquare) 2-HDEAB and (\diamondsuit) 2-HDEAP

Dyeing procedure, color measurement and other quality parameters

Reactive dyes differ from others in that they react chemically with the textile fiber, forming strong covalent bonds between the dye molecules and the fiber-forming polymer. However, a disadvantage of conventional reactive dyestuffs lies in the fact that the unfixed dye undergoes hydrolysis, instead of reaction with the fabric.¹³¹⁻¹³⁴ This hydrolyzed dye is unable of forming bonds with the fiber and reduces the wet fastness properties, if not removed fully during washing.⁶⁰ To increase the chemical affinity between the dye molecules and the tested fibers, a high-fixation hetero-functional dyestuff (Drimaren Yellow CL – 2R), containing two reactive groups (monochlorotryazine – MCT, and vinylsulfone – VS) and three solubilizing groups, has been used, and the dyeing step was preceded by a cationization process. According to Shu *et al.*,¹³⁵ the higher the molecular mass per soluble group, the higher the fixation rate.

Dyeing cationized fibers results in greater fixation of the dye and higher K/S values. In addition, the strong dye-fiber interactions resulting from cationizing fabric allow dyeing to be accomplished with no added chemicals and minimal rinsing and after-washing. In a typical cationization process, the cationic sites on the modified fiber strongly attract anionic dye molecules, leading to performance and process improvements.¹³⁶ The quaternary ammonium group, $-N(CH_3)_3^+$, contained in the cationizer, has a persistent positive charge and can thereby lead to the formation of ionic bonds with negatively charged anionic groups, such as those found in a wide array of anionic dye classes or carboxyl compounds. The mechanism for dyeing cationized cotton, polyamide and wool fibers in water with reactive dye is well known.⁵²⁻⁵⁵ Figure 15 shows, as an example, the dyeing mechanism of cationized cotton fiber using protic ionic liquids. In this non-aqueous ionic medium, the process can be described by an initial etherification reaction between the hydroxyl group of the fabric surface and the epoxide group of the cationizer in alkaline medium (Fig. 15 a-b). Under alkaline conditions, CHPTAC forms EPTAC (2,3-epoxypropyl trimethylammonium chloride), which further reacts with the fiber to form ether linkages. However, EPTAC can also undergo hydrolysis under alkaline conditions to form an unreactive-diol compound¹³⁷⁻¹³⁸ (Fig. 15c). The fixation efficiency is observed to decrease with increasing liquor ratio and temperature, because EPTAC hydrolysis reaction is more favorable at higher quantities of water and higher temperature.¹³⁹ Additionally, higher fixation of the cationizing agent can be obtained by using additives, such as ethanolamines and carboxyl acids, as they tend to form complexes with CHPTAC, thus reducing the hydrolysis reaction.¹³⁷ Thus, it can be deduced that, in a non-aqueous medium, at moderate temperatures and in the presence of ethanolamine-based ionic liquids, EPTAC hydrolysis is reduced and there is a higher yield in this stage.

The cationic sites (ammonium groups) create a strong positive potential in the dyebath, during which the anionic nucleophilic reactive dye molecules move from the dyebath medium to the fiber. Due to the high substantivity of cationic sites in the cationized fabric to the anionic nucleophilic dve molecules, they readily interact to form a strong ionic bond between them, even without the addition of alkali for the fixation process.¹⁴⁰ The mechanism for fixation of reactive dye on the cationized fiber is not only by the formation of this ionic bond between the cationic sites with the anionic nucleophilic dye molecules, but also by the formation of a covalent bond between the leftover primary hydroxyl groups of the fiber with the anionic group of reactive dye molecules, as shown in Figure 15d.¹⁴¹⁻¹⁴² At this stage, the protic ionic liquids as dyeing medium both increase the wettability of the fabrics, acting as dve carrier, and contribute to the ionization of the dye's reactive groups (in this case, monochlorotriazine and vinylsulphone). In addition, this non-aqueous medium completely prevents the dye hydrolysis, which can occur as a result of its interaction with the hydroxide in water.¹⁴² As shown in Figure 15e, this hydrolyzed dye is unable of forming bonds with the cellulose and reduces the wet fastness properties, if these hydrolyzed dyes are not fully removed during the washing stage. Multiple soaping and rinsing steps are usually required after the dyeing process in order to remove these hydrolyzed dyes.

This explained mechanism is similar for polyamide and wool fibers. Polyamide contains many amide groups in its structure. It also contains free amine groups at the ends of its polymeric chains, although the number of these free amine groups is lesser than the number of carboxylic groups. Amino groups are alkaline and carboxylic acids are in acidic form easily capable of being linked. Wool belongs to a group of proteins known as keratins. It has a heterogeneous composition, where the protein is made up of amino acids and acidic carboxyl groups. Instead of EPTAC reacting with OH groups on the cotton surface, it reacts with NH_2 and COOH groups on the polyamide and wool surfaces. The rest of the process follows the same mechanism as that detailed for cotton above.



Figure 15: Cationization and cotton dyeing mechanism using a (monochlorotriazine + vynil sulfone) based reactive dye and protic ionic liquids as dyeing medium



Figure 16: Color measurement analysis of K/S (ratio between absorption coefficient and dispersion coefficient) for multifiber fabrics cationized and dyed with reactive dye using 4 different PILs as solvent

On the other hand, reactive dyes are rarely employed for diacetate, polyester and acrylic fibers. Usually, these dye molecules cannot easily penetrate the highly ordered internal structures of these synthetic fibers. In the absence of high temperatures and specific carriers, dye adsorption normally takes place only in the less-ordered regions and on the surface of crystalline regions.⁴¹ In these cases, disperse dyes are commonly applied. Due to its highly insoluble character in water, the initial diffusion of the dye onto the fiber surface is preceded by the dissolution of the disperse particles above 100 $^{\circ}C$.¹⁴³

With the aim of analyzing the possibility of using a "universal dye", in this study, we have tested the cationization of diacetate, polyester and acrylic fibers, to enable them to be dyed with the same reactive dye. It is expected that the cationizer-fiber interaction mechanism will be similar to the one previously described.

Cellulose diacetate is a synthetic polymer made by treating cellulose with acetic acid. It consists of two acetyl functional groups on each unit of D-anhydroglucopyranose of the cellulose molecule. The polyester used belongs to a category of polymers called polyethylene terephthalate (PET), which contain the ester functional group in their main chain. Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with about 1900 monomer units, usually vinyl acetate or methyl acrylate. Instead of EPTAC reacting with OH groups on the cotton surface, it could react with acetate, oxide or cyanide anions on the diacetate, polyester and acrylic fibers, respectively. The rest of the process follows the same mechanism as that detailed for cotton. Figure 16 shows the obtained K/S values for the cationized and dyed samples previously indicated.

As shown, all the fibers underwent a color change (positive values of K/S). In general terms, it is possible to observe that PILs with longer anions provided higher K/S values for each fabric (see diacetate, acrylic or wool sequences in Fig. 16). A possible explanation is the probably higher capability of these PILs to change the exposed surfaces of fiber structure,¹⁴⁴⁻¹⁴⁵ promoting better dye insertion into the fiber. Additionally, lower values of density and surface tension of these higher molar mass PILs may allow for an improvement in the wettability of the fabric, a key factor for good dyeing.¹⁴⁶ Cationized cotton fabrics dyed in 2-HEAA, 2-HDEAPr and 2-HDEAB, previously tested as dyeing media, exhibited higher K/S values than those previously published for uncationized cotton fabrics dyed with a similar reactive dye under the same process conditions,⁸⁶ which reinforces the efficiency of the pre-cationization process.

Regarding fabrics, synthetic fibers with diacetate and acrylic groups presented the best results. However, it is necessary to be careful with the values provided by this K/S parameter. High K/S values can indicate both high quality dyeing and, simultaneously, an extremely bright color. As previously discussed (Andrade *et al.*, 2017),⁸⁶ low K/S values, but higher perceptual color, compared with the blank samples, should be justified by the differences in lightness and darkness ($\Delta L^* = L^*$ sample

minus L* standard), *i.e.*, these samples can exhibit a "stronger yellow color", but a brighter appearance (far from black – value 0 – and next to white – value 100 – in the color space) (Fig. 17), which results in increased reflectance, then decreasing the K/S value.

As seen, ΔL values of the two synthetic fibers with the highest K/S values (acrylic and diacetate) are the highest among those analyzed, indicating that these samples acquired a whitish appearance when dyed in all tested PILs. To illustrate the real acquired hue for each fiber, the color intensity was analyzed according to the Color Measurement Committee (CMC, UK). Figure 18 shows these visual results. In this case, wool and cotton have the highest visual intensity color acquired among the multifiber fabrics. Here, the higher influence of protic ionic liquids of greater anion on the dyeing quality is proven.

Figure 19 shows the obtained color difference (ΔE parameter) for each fiber. On a typical scale, the ΔE value ranges from 0 to 100, and different values mean different human perceptions.¹⁴⁷ In the case of CIE 76 used formula,¹⁴⁸ $\Delta E \le 1.0$ is not perceptible by human eyes, $1 < \Delta E \le 2$ is perceptible through close observation and $2 < \Delta E \le 10$ is perceptible at a glance. ΔE greater than 50 is highly perceptible to the human eye, and the closer to 100 the value, the more opposed in the color space are the samples compared.

Reinforcing what was noted earlier, PILs with longer anionic carbon chains reach better ΔE results, with values ranging from 39.80 for polyester to 51.33 for cotton fiber dyed in 2-HDEAP, and from 36.78 for polyester to 55.01 for cotton fiber dyed in 2-HDEAB. The lowest value (31.88) was observed for dyed polyester in 2-HDEAPr. Anyway, according to the Commission Internationale de l'Eclairage (CIE) and to industry standards, all the results obtained are satisfactory and noticeable to the human eye.¹⁴⁹

In addition, the perceptual color and the dyeing quality could also be evaluated by analyzing the CIE L*a*b* color space. Figure 20 shows a* and b* color coordinates for the dyed samples. The graph is a conventional two-dimensional CIEL*a*b* color space plot, where the abscissa shows +a* (at the right) – the red color and, when necessary, could also show -a* (at the left) – the green color. Similarly, the ordinate shows +b* (at the top) – the yellow color and, when necessary, could also show -b* (at the bottom) – the blue color.



Figure 17: Differences in lightness and darkness (ΔL* = L* sample minus L* blank) for each fiber dyed using (●) 2-HEAA, (■) 2-HDEAPr, (▲) 2-HDEAB and (★) 2-HDEAP





Figure 18: Processed images by DATACOLOR™ 550 spectrophotometer according to its respective CMC measured values

Figure 19: Color difference between standard (fibers analyzed before dyeing) and dyed sample (ΔE), related to the solvent used



Figure 20: Conventional two-dimensional CIE L*a*b* color space plot for the dyed samples



Figure 21: Grey scale analysis, which determines the color change compared with fabric before testing (from the left (highest color difference) – to the right (no color difference)

The coloration trends observed are produced by three factors, the fabric type, the medium in which the dyeing is carried out and, finally, the operational conditions applied during the process. Obviously, since the dye used was Drimaren Yellow CL-2R (Clariant), the dying quadrant will be that showing positive values for the parameters a* and b* (upper right quadrant in Fig. 20). In all the cases, an approximately linear tendency (2-HDEAA < 2-HDEAPr < 2-HDEAB < 2-HDEAP) was observed when comparing the ionic media used in the dyeing process (see inset in Fig. 20), allowing us to conclude that longer chain PILs impart to the fabric a color hue closer to red and yellow (the larger the anion, the greater a* and b* coordinates). As already mentioned, this graph cannot be interpreted by itself, since higher values of a* and b* associated with low L* values can result in unsatisfactory quality colors. Higher +b* ("more yellow color") values associated with lower L* (dark appearance) values were obtained for cotton fibers.

The color fastness properties of cationized multifiber fabrics dyed with reactive dye were evaluated

in terms of fastness to rubbing and perspiration. The grey scale was used for comparison, which varies from number 1, which indicates the highest color difference, to number 5, which means no color difference.¹⁴⁹ Figure 21 shows an example of the grey scale and the assessment of color fastness, where the worse result is on the left side of the figure and the best result (no color difference) is on the right side.

As for the color transfer test, both under dry and wet conditions, all the classes of fibers submitted to dyeing in the 4 tested PILs as dyeing solvents showed analogous behaviour. All the fibers obtained classification 5, and there was no significant color transfer from the dyed fabric to a control sample, which confirms the quality of dyeing and the high level of fixation of the reactive dye onto the tested fabrics. Also, from the results of the perspiration test, it could be observed that the dyed samples show good color fastness properties for cationized dyed fabrics (most 4-5/5 units on the grey scale, whereas 5 is the best grade). This result can be explained by the affinity of cationized multifiber to reactive dye, as well as the efficiency of the mechanism of dye diffusion and chemical bonding on fabrics in ionic environment.

CONCLUSION

Continuing previous research, in this paper, we present a non-pure-aqueous procedure for textile dyeing, testing different types of fabrics, with a polyfunctional reactive dye and protic ionic liquid (PIL) as reaction medium, with cationization pretreatment of the tested fibers. To analyze the effectiveness of the procedure, currently established dyeing quality parameters, such as color absorption and wash fastness of the dyed multifiber fabrics have been measured and analysed.

Considering the obtained results, the following conclusions could be drawn:

1) A thermodynamic/spectrometric characterization of the protic ionic liquid 2-hydroxy diethylammonium butanoate (2-HDEAB) was realized. New measurements of density, ultrasonic velocity, refractive index, surface tension, dynamic viscosity and ionic conductivity as a function of temperature, as well as different derived magnitudes, were made and found to be consistent with previous data obtained for the functional family of protic ionic liquids and other earlier published data. NMR spectroscopy confirmed the main functional groups of the ionic compound.

2) The performance of a new proposed method for dyeing diacetate, cotton, polyamide, acrylic and wool fibers, avoiding the use of several chemical additives and large amounts of water, was analysed. This process involved a cationization pretreatment of the tested fabrics and non-aqueous dyeing using protic ionic liquids (2-hydroxy diethylammoniumacetate (2-HDEAA), 2-hydroxy diethylammonium propionate (2-HDEAPr), 2-hydroxy diethylammonium butanoate (2-HDEAB) and 2-hydroxy diethylammonium pentanoate (2-HDEAP) as the only solvent media and a polyfunctional reactive dye, Drimaren Yellow CL-2R (Clariant), which contains a combination of triazines and vinyl sulfone groups, with fixation and solubilization functions, respectively.

3) The mechanism for dyeing cationized cotton, polyamide and wool fibers in water, with reactive dye, is usual and well known. Reactive dyes are rarely employed for diacetate, polyester and acrylic fibers, as these dye molecules cannot easily penetrate the highly ordered regions of these synthetic fibers in the absence of high temperatures and specific carriers. It can be deduced that in a non-aqueous medium, at moderate temperatures and in the presence of ethanolamine-based ionic liquids, EPTAC hydrolysis is significantly reduced and there is a higher yield at this stage. Despite these facts, in search of a "universal dye" for all kinds of fibers that can represent a significant innovation in the textile chemistry, to reduce the dyeing process complexity and wastewater treatment, this new proposed method for dyeing was analyzed under different operational conditions.

4) Color measurement and other quality parameters were determined on the tested fabrics. Color strength of the dyed fabric samples was analyzed by using a DATACOLORTM 550 spectrophotometer (450 nm). Based on the readings of reflectance, the values of K/S were calculated by using the Kubelka–Munk equation. In addition to the reflectance values, the spectrometer provides the tristimulus values (X, Y, Z), which were then transformed into the L*a*b* color space. Additionally, the color intensity was measured according to the Color Measurement Committee (CMC, UK), defined by a set of well-known equations from a large study of the acceptability of color differences in all regions of the color space. In general terms, it is possible to observe that PILs with longer anions provided higher K/S values. Lower values of density and surface tension of these higher molar mass PILs may allow for an improvement in the wettability of the fabric, a key factor for a good

dyeing. Reinforcing what was noted earlier, PILs with longer anionic carbon chains enable better ΔE results, according to the Commission Internationale de l'Eclairage (CIE) and to industry standards. All the results obtained are satisfactory and noticeable to the human eye. An approximately linear tendency (2-HDEAA < 2-HDEAPr < 2-HDEAB < 2-HDEAP) was observed when comparing the ionic media used in the dyeing process, allowing us to conclude that longer chain PILs impart to the fabric a color hue closer to red and yellow (the larger the anion, the greater a* and b* coordinates).

5) The color fastness properties of cationized multifiber fabrics dyed with reactive dye were evaluated in terms of fastness to rubbing and perspiration. For the color transfer test both in dry and wet conditions, all classes of fibers submitted to dyeing in the 4 PILs as dyeing solvents showed analogous behaviour. All the fibers obtained classification 5, and there was no significant color transfer from the dyed fabric to a control sample, which confirms the quality of dyeing and the high level of fixation of the reactive dye into fabric. Also, from the results of the perspiration test, it could be observed that the dyed samples show good color fastness properties for cationized dyed fabrics (most 4-5/5 units on the grey scale, whereas 5 is the best grade).

6) The obtained dyeing results should be explained by the affinity of cationized multifiber to the reactive dye, as well as the efficiency of the mechanisms of dye diffusion and chemical bonding on the tested fabrics in protic ionic liquid environment. In addition to increasing the final quality of the dyeing, the presence of cationized groups in the fabric also imparts antimicrobial properties and reinforces the efficiency of the dyeing process, minimizing dye loss and unnecessary complex washing stages.

The obtained results performed well when compared with standard dyeing quality parameters in earlier published literature, under the same operational conditions, opening opportunities for innovation and optimization, rethinking the industry, taking care of the people who work in it and of the environment, focusing both on processes and results, trying to create a better future in all aspects.

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Abbreviations

PIL, Protic Ionic Liquid; 2-HDEAA, 2-Hydroxy Diethylammonium Acetate; 2-HDEAPr, 2-Hydroxy Diethylammonium Propionate; 2-HDEAB, 2-Hydroxy Diethylammonium Butanoate; 2-HDEAP, 2-Hydroxy Diethylammonium Pentanoate; CIE, The Commission Internationale de l'Eclairage; ABNT, Associação Brasileira de Normas Técnicas; CMC, Color Measurement Committee

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