

# Sustainable Cotton Dyeing in Nonaqueous Medium Applying Protic Ionic Liquids

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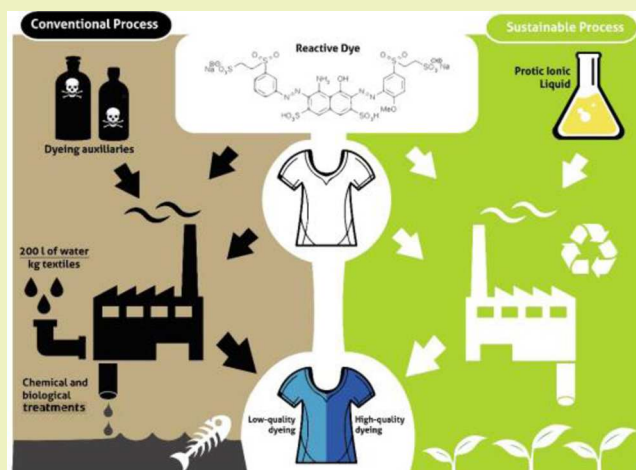
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## S Supporting Information

**ABSTRACT:** Dyeing processes are highly important for differentiation of textile products, and in general, they use a huge amount of water and chemical additives, generating a great environmental impact. In the last years, the interest in finding alternative environmentally friendly solvents for these processes has increased, with a double aim: to decrease the quantity of water used and to improve the dyeing quality. In this work, we analyze an alternative procedure to dye cotton fabrics with only two dyeing agents, a polyfunctional reactive dye and a protic ionic liquid (PIL) as an alternative solvent, avoiding the need for common chemical additives into the conventional process, thus reducing the amount and concentration of pollutants. The proposed procedure allows PIL recycling with no appreciable loss of efficiency, since after dyeing, the unfixed dye remains active in the bath, following the known exhaustion dyeing method. A collection of 13 PILs were studied with the aim of analyzing their effectiveness as dyeing solvents in terms of different standard dyeing quality parameters such as absorption color, tensile strength, and surface morphology of the cotton dyed. The results obtained using PIL as dyeing solvents in the absence of any auxiliary agent showed an outstanding effect when compared with the aqueous process under the same operational conditions.

**KEYWORDS:** Protic ionic liquid, Sustainable textile dyeing, Cotton, Reactive dye



## INTRODUCTION

The dyeing process is known in the textile industry as the aqueous application of dyestuffs or pigments to textile substrates, mainly using synthetic agents and chemical additives to get fastness properties suitable for the end use of the fabric.<sup>1–3</sup> The textile industry uses approximately 200 L of water to process each kilogram of textiles<sup>4</sup> producing outstanding quantities of wastewater and severe environmental impacts.<sup>5</sup>

Many of the applied chemicals in this process are highly toxic and not easily biodegradable. For example, the azo and nitro dyes may be metabolized to carcinogenic agents and affect the

photosynthetic function in plants.<sup>6</sup> Nonylphenol ethoxylates (NPEs) are used as surfactants and detergents<sup>7</sup> and should be metabolized to nonylphenols (NPs), a toxic and hormone-disrupting substance,<sup>8</sup> impacting directly on the environment and/or human health. So, textile effluents must be treated before discharge according to the wastewater character and discharge limits, and different processes (physical, chemical, biological) must be applied for an adequate treatment of textile

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wastewater. Conventional remediation methods, like oxidation and cavitation,<sup>9–11</sup> physical,<sup>12–14</sup> and biological<sup>15–17</sup> wastewater treatments present disadvantages and, at the same time, high cost and low decolorization efficiency.<sup>6,18</sup>

In the last years, with the aim of reducing water and chemical consumption and waste discharge, some procedures employing nonaqueous dyeing processes have been proposed like use of supercritical carbon dioxide as a dyeing medium,<sup>19–21</sup> solubilization and adsorption of direct dyes into aerosol reverse micellar system,<sup>22</sup> and sorption of disperse dyes on polylactic acid (PLA) fibers in nonaqueous medium,<sup>23</sup> mainly due to economic factors, the conventional and noneco-friendly dyeing processes using aqueous basis remain largely employed worldwide until now.

Ionic liquids (ILs) are a new family of solvents that are being used in a large variety of applications because of an amazing number of desirable properties.<sup>24–26</sup>

Recent papers have shown that ILs gather potential to be used in some textile innovative processes.<sup>27–29</sup> However, there are some main problems with these new substances, such as their low biodegradability<sup>30,31</sup> and expensive production costs which makes their industrial implementation difficult.

The studied ionic liquids into this work belongs to a newly designed class, the protic ionic liquids (PILs),<sup>32,33</sup> substances potentially biodegradable<sup>34–36</sup> and based amines as cations and organic deprotonated acids as anions<sup>26,36</sup> without potentially hazardous molecular groups.

Reactive dyes are an important class of chemicals for cotton dyeing. They are capable of forming chemical covalent bonds with the cellulose fiber<sup>37</sup> and, therefore, better anchored to the substrate and not depending on the relatively weak physical forces to give better levels of fastness. Dyestuffs containing two (bifunctional dyes) or more (polyfunctional dyes) different reactive groups were developed to increase the degree of fixation.

In this study, we analyze the performance of a system formed by only two agents (PIL + reactive dye), for dyeing cotton fibers, avoiding the use of several chemical additives and large amounts of water. The used polyfunctional reactive dye was the Marinho Sidercron, containing a combination of triazines and vinyl sulfone groups, with fixation and solubilization functions. This dye is more tolerant to temperature deviations and offers fastness (better quality) in the dyeing process. With the aim of analyzing their effectiveness as dyeing solvents, a collection of 13 PILs of different chemical structures were studied in terms of physicochemical properties. The dyeing properties and other functional properties important to textile applications are reported. The proposed process allows recycling PIL after the dyeing step, the unfixed dye remains in the dyeing bath and should be reused into a new process diminishing dye make up with no appreciable ionic solvent loss of efficiency.

## EXPERIMENTAL SECTION

**Protic Ionic Liquid Synthesis.** The amine compounds (Merck Synthesis, better than 99%) were placed in a flask equipped with a reflux condenser, a temperature sensor for controlling temperature, and a dropping funnel. The organic acid (Merck Synthesis, better than 99%) was added dropwise to the flask under stirring with a magnetic bar.

The reaction is a Bronsted reaction, creating a salt of mono- or diethanolamine, namely 2-hydroxy diethylammonium acetate (2-HDEAA), 2-hydroxy diethylammonium formate (2-HDEAF), 2-hydroxy diethylammonium lactate (2-HDEAL), 2-hydroxy diethylammonium maleate (2-HDEAMA), 2-hydroxy diethylammonium

oxalate (2-HDEAOx), 2-hydroxy diethylammonium propionate (2-HDEAPr), 2-hydroxy diethylammonium salicylate (2-HDEASa), 2-hydroxy diethylammonium succinate (2-HDEASu), 2-hydroxy ethylammonium acetate (2-HEAA), 2-hydroxy ethylammonium adipate (2-HEAAD), 2-hydroxy ethylammonium citrate (2-HEACi), 2-hydroxy ethylammonium lactate (2-HEAL), and 2-hydroxy ethylammonium propionate (2-HEAPr). This collection of PILs was designed attending to two main objectives, analyze the effect of a progressively greater anion (from 2-HDEAF to 2-HDEASa) and the effect of different number of active sites in the ions (from 2-HEAA to 2-HEACi).

The specific chemical structure of each PIL should be found as [Supporting Information](#).

The perceptual color varies in each case from transparent to dark yellow when the purification process (strong agitation and slight heating for vaporization of residual nonreacted amine at low pressure) was completed.

At each case, after synthesis, spectrometry (RMN and FT-IR) and thermodynamic measurements were made in order to ensure purity of the product before experimental measurements and dyeing analysis in our lab.<sup>38–43</sup>

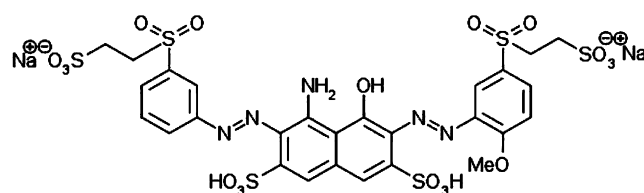
**Physicochemical Property Measurements.** The pure PILs were stored in sun light protected form, constant humidity, and controlled temperature in our laboratory. The usual manipulation in our experimental work was applied.<sup>42,43</sup> The densities and ultrasonic velocities of pure components were measured with an Anton Paar DSA-5000 vibrational tube densimeter and sound analyzer, with a resolution of  $10^{-5}$  g cm<sup>-3</sup> and 1 m s<sup>-1</sup>.

The stress–strain flow behavior of the PILs was determined using an AR2000EX rheometer (TA Instruments, New Castle, DE) with stainless steel cone and plate geometry with a diameter of 52 mm and a 2° cone angle. The curves were obtained with a shear rate ranging from 0 to 100 s<sup>-1</sup>, during 120 s, at 298.15 K, in triplicate. The temperature was controlled ( $\pm 0.1$  K) by a standard circulation water of the equipment (Peltier plate), able to control the temperature of the plate geometry, and thus, of the sample.

The pH was measured by a Jenway 3540 pH/conductivity meter with resolution of 0.01 pH and accuracy of  $\pm 0.5\%$  at the measured temperature (298.15 K).

Detailed description of our experimental procedure on thermodynamic properties measurements should be found in earlier published works.<sup>41–43</sup>

**Dyeing Procedure.** The dyeing process was carried out with cotton fabrics (100% CO) and a polyfunctional reactive dye Marinho Sidercron (chemical structure is shown in [Figure 1](#)), which was



**Figure 1.** Chemical structure of a polyfunctional reactive dye Marinho Sidercron.

provided by Siderquímica, Paraná, Brazil. The dye concentration was 2% w.w. (cotton fabric weight: dye weight); the ratio R:B (cotton fabric weight versus bath weight) was fixed in 1:20, and the dyeing temperature was set at 333.15 K, according to the common practice of cotton dyeing industrial process.

Experimental dyeing tests were developed into a all-in-glass temperature controlled reactor using a static direct contact procedure.<sup>44,45</sup> Initially, the reactive dye is added to the reactor with PIL in the previously indicated ratio, initiating the heating process and progressive solubilization for 15 min by mechanical stirring with an external temperature control bath. After this time, the fabrics were added in pairs to the dyeing reactor. The dyeing time was fixed in 60 min in order to reach the highest coloristic intensity values. Each pair

of samples was dyed using a specific PIL, and then the fabrics were washed off using standard detergent aqueous solution (1 g/L) at a liquor ratio of 20:1 (aqueous wash solution weight versus cotton fabric weight) for 30 min at 298.15 and 333.15 K, each sample being washed at each temperature to compare the effect of the temperature in the dyeing quality. After complete removal of PIL and unfixed dye in the fabric, all samples were dried at ambient temperature by natural convection and constant humidity. Blank experiments were carried out under identical conditions, replacing PIL by the equivalent quantity of water for comparison and analysis of improvement of PIL dyeing.

**Color Measurements.** Reflectance measurements were applied to determine the color strength of the dyed samples, which were directly monitored at the wavelength of maximum reflectance, determined from the recorded reflectance spectra in the wavelength range from 400 to 700 nm. The color strength of the dyed fabric samples was analyzed by using a DATACOLOR 550 spectrophotometer. Based on the readings of reflectance for the samples at 490 nm,  $K/S$  values were computed by using the Kubelka–Munk equation (eq 1).

According to the literature, there exists a well-established linear dependence of  $K/S$  on the color of a solid surface:<sup>46</sup>

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

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

In addition to reflectance values, the spectrometer provides the tristimulus values ( $X$ ,  $Y$ ,  $Z$ ), which were then transformed into the  $L^*a^*b^*$  color space, according to eqs 2–10. Defined by the Commission Internationale de l'Éclairage (CIE), in the  $L^*a^*b^*$  color space (CIELAB) the parameter  $L^*$  indicates lightness,  $a^*$ , the red/green coordinate, and  $b^*$ , the yellow/blue coordinate.

$$L = 116(f_y - 16) \quad (2)$$

$$a = 500(f_x - f_y) \quad (3)$$

$$b = 200(f_y - f_z) \quad (4)$$

where

$$f_x = \begin{cases} \sqrt[3]{x_r} & x_r > \varepsilon \\ \frac{kx_r + 16}{116} & x_r \leq \varepsilon \end{cases} \quad (5)$$

$$f_y = \begin{cases} \sqrt[3]{y_r} & y_r > \varepsilon \\ \frac{ky_r + 16}{116} & y_r \leq \varepsilon \end{cases} \quad (6)$$

$$f_z = \begin{cases} \sqrt[3]{z_r} & z_r > \varepsilon \\ \frac{kz_r + 16}{116} & z_r \leq \varepsilon \end{cases} \quad (7)$$

and

$$x_r = \frac{X}{X_r} \quad (8)$$

$$y_r = \frac{Y}{Y_r} \quad (9)$$

$$z_r = \frac{Z}{Z_r} \quad (10)$$

where  $X_r$ ,  $Y_r$ , and  $Z_r$  are reference coordinates (measured from a reference sample, dyed into the conventional aqueous medium, without PIL), and the parameters  $\varepsilon$  and  $k$  are standard values fixed by CIE.

**Mechanical Properties of Samples.** A tensile test is a fundamental mechanical validation where a sample is loaded while measuring the applied load, as well as, its elongation over a distance. Tensile tests can be used to determine mechanical properties as elongation, tensile strength and other tensile properties.

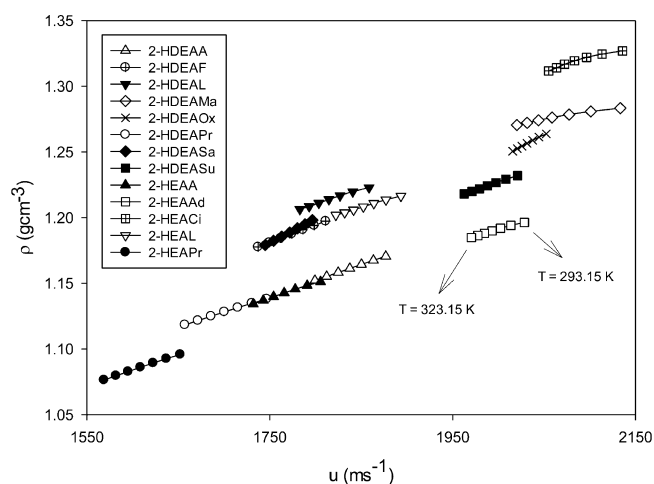
The cotton textile industry must deliver fibers that provide an optimized fabric for textile manufacturing in order to compete effectively with other synthetic fibers.<sup>47</sup> The strength/elongation properties that determine the amount of energy (often called the work-to-break) required to break either a fiber or a yarn and work-to-break is critically important to processing performance. Many studies have shown the importance of fiber elongation and its contribution to yarn quality and specifically to yarn toughness or work-to-break values.<sup>48,49</sup> Tensile resistance tests were performed on a dynamometer (MAQTEST) with a 10 kgf load cell, and the tensile resistance and strain at break of the fabrics were determined following ASTM D5035-95 method. The specimen gauge length used was 100 mm, with the cross-headspeed fixed at 200 mm min<sup>-1</sup>.

**Surface Morphology of Samples.** Due to the ability of atomic force microscopy (AFM) to image surfaces in any environment without sample pretreatment, the applications of this technique for research of materials and surface science have grown in recent years.<sup>50</sup> The AFM is an adequate tool for textile studies because it provides information on both the fundamental surface forces (in terms of fiber–dye interaction) and on fabric roughness gain through topographic images. Several comprehensive reviews exist detailing the extensive use of AFM for the analysis and characterization of textiles, such as early studies performed on the surfaces of cotton<sup>51</sup> and polyester<sup>52</sup> treated fibers.

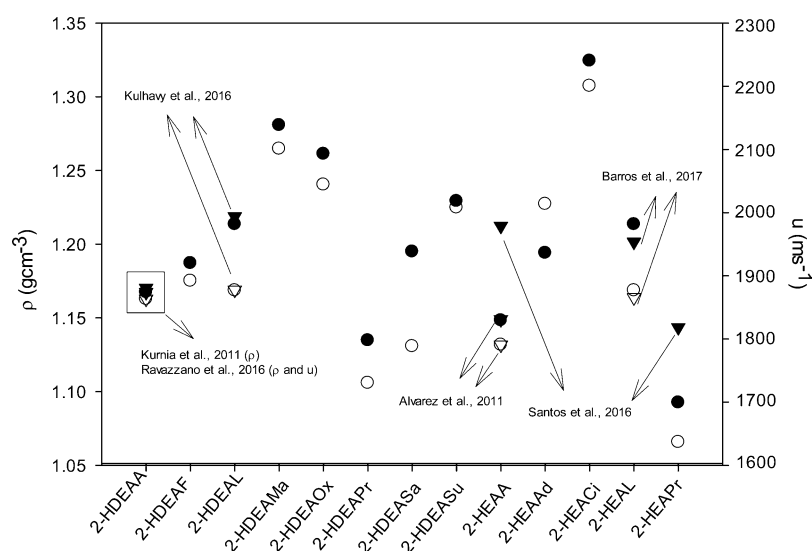
The surface morphology of nondyed cotton treated with PILs (under identical conditions of the explained dyeing process, but without dye, in order to not interfere with the analysis of the PILs influence on the fabric fiber, and cool-washed) was examined using a Bruker's Dimension Icon atomic force microscope, in the intermittent contact mode. The sample surface was analyzed using a silicon probe, which covered an area of 5  $\mu\text{m} \times 5 \mu\text{m}$  at a frequency of 1 Hz. Data acquisition and analysis were carried out using the WSxM software.

## RESULTS AND DISCUSSION

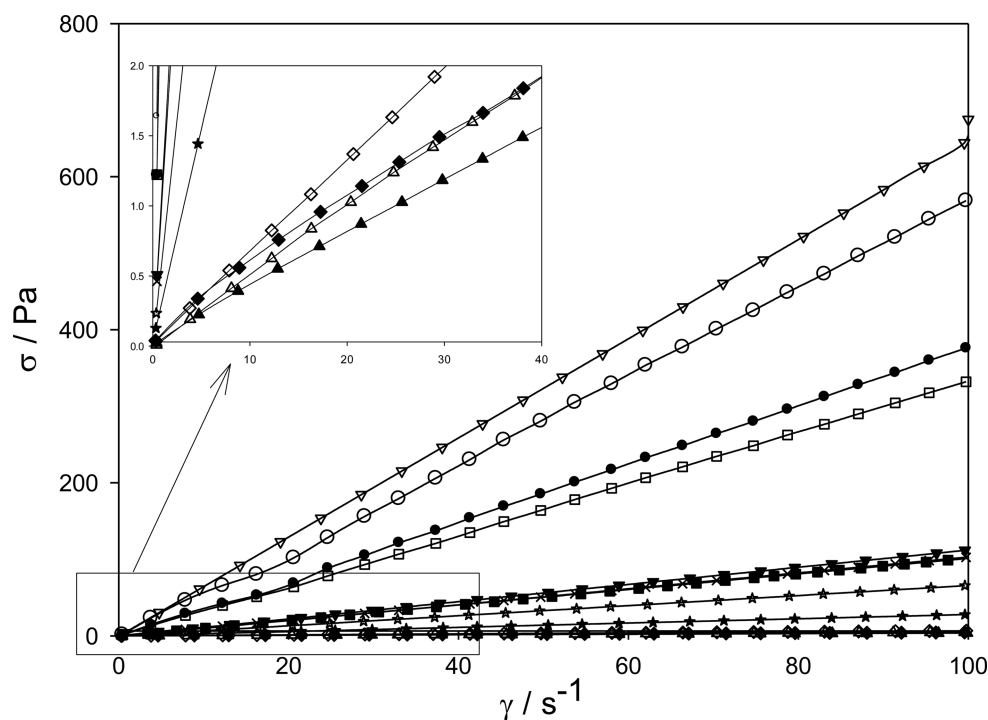
**Spectrometric and Physicochemical Characterization of Protic Ionic Liquids.** Both Fourier transform infrared (FT-IR) and <sup>1</sup>H-NMR spectra indicate a salt structure of the synthesized protic ionic liquids. In the IR spectra the broad band around 3500–2400 cm<sup>-1</sup> implies the known ammonium structure. The ester group bonding vibrations are observed as a



**Figure 2.** Density ( $\text{g cm}^{-3}$ ) versus ultrasonic velocity ( $\text{m s}^{-1}$ ) experimental measurements for all the studied PILs at a range of temperature 293.15–323.15 K.



**Figure 3.** (●) Density ( $\text{g cm}^{-3}$ ) and (○) ultrasonic velocity ( $\text{m s}^{-1}$ ) experimental measurements for all the studied PILs at 298.15 K and literature data for comparison (▼ for density and ▽ for ultrasonic velocity).



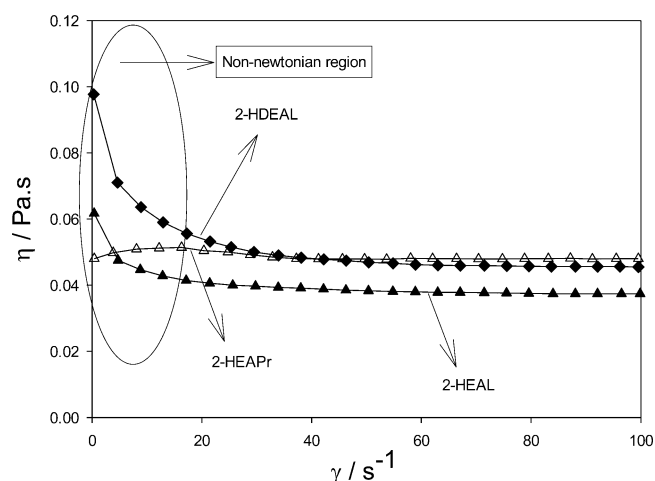
**Figure 4.** Shear stress (Pa) versus shear rate ( $\text{s}^{-1}$ ) curves at 298.15 K of (▼) 2-HDEAA, (◇) 2-HDEAF, (◆) 2-HDEAL, (▽) 2-HDEAOx, (●) 2-HDEAMa, (☆) 2-HDEAPr, (□) 2-HDEASa, (■) 2-HDEASu, (★) 2-HEAA, (×) 2-HEAAAd, (○) 2-HEACi, (▲) 2-HEAL, and (△) 2-HEAPr. Solid lines are the fitted curves.

combined bond centered around  $1600 \text{ cm}^{-1}$ . In the NMR analyses, signals of the adjacent methylene protons to the nitrogen atom and OH groups are observed. The FT-IR and  $^1\text{H-NMR}$  spectra (Figures S1–S39 and Tables S1–S13) and a detailed description about the spectrometric characterization of the 13 studied PILs are given as [Supporting Information](#).

Knowledge of thermodynamic properties of fluids (volumetric, sonic, calorimetric or rheologic characterization) is valuable for textile industries in terms of predicting their performance in a dipping and stirring operation and the ease with which they should be applied. In dyeing processes, it is necessary to maintain different physicochemical properties of

the dye bath around acceptable values. Increasing values of density and viscosity could result in a radical reduction of fabric wettability and, consequently, in the loss of final dyeing quality. As it happens with other thermodynamic properties, an enormous gap of information occurs in the open literature in terms of density, ultrasonic velocity, viscosity, or any other parameters of ionic liquids. Only in the past few years has a relative increase of the number of papers devoted to these measurements been observed. A simple search into any popular scientific finder paints a bleak picture for PILs. The experimental measurements of density and ultrasonic velocity as a function of temperature and the isentropic compressibility





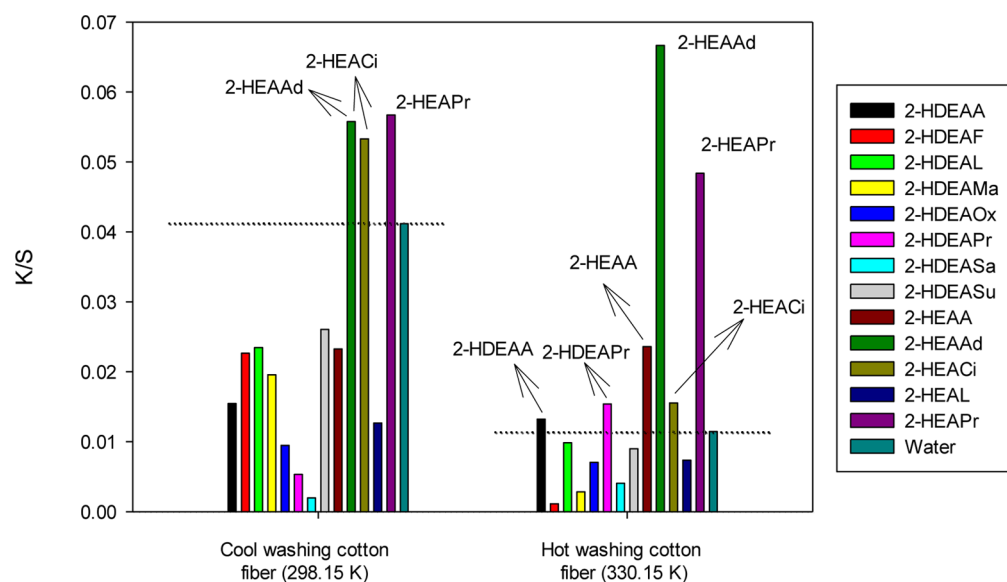
**Figure 5.** Dynamic viscosity (Pa s) versus shear rate ( $s^{-1}$ ) at 298.15 K for (♦) 2-HDEAL, (▲) 2-HEAL, and (△) 2-HEAPr. Solid lines are the fitted curves.

(derived from the Laplace–Newton equation) (Supplementary Table S14 and Figure 2) provide us a preliminary characterization of the PILs, with deviations between experimental and literature data<sup>41,42,53–56</sup> lower than 6% for density and 8% for ultrasonic velocities (Figure 3). For all the studied PILs, it was observed that the increase of temperature diminishes the ion–ion interactions, increasing kinetics and producing lower values of density and ultrasonic velocity for higher temperatures in each case. The organic residual chains in the ions building each PIL have strong effects on the physicochemical properties, the steric hindrance being a relevant factor for accommodation into a liquid net.<sup>39</sup> The factors studied are the chain length into anion and the substitution degree into cation. Their effect depends strongly on the nature of ions, but the influence of the anion aliphatic residue seems higher, due to its longer structure producing a stronger disturbance in terms of accommodation of the ionic bulk structure. In terms of rheological behavior, Figure 4 gathers the flow curves of the studied PILs at 298.15 K,

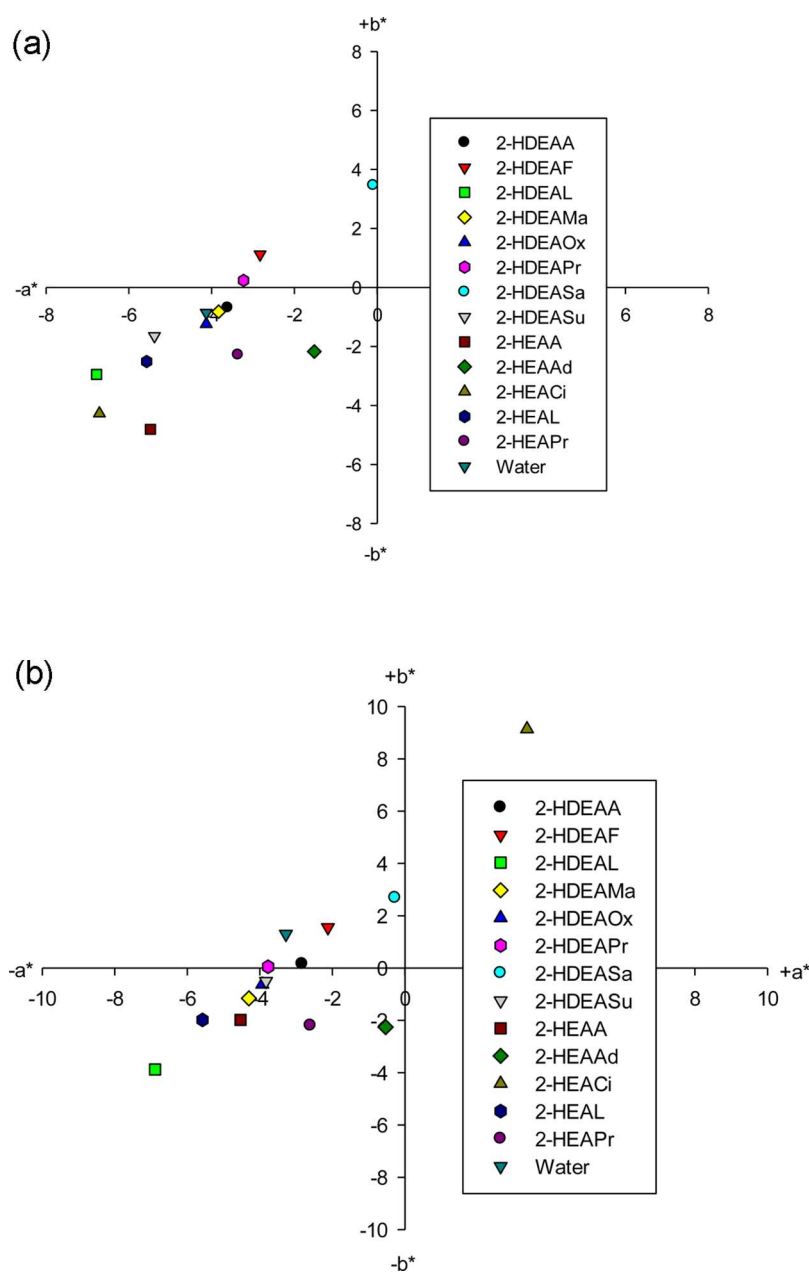
obtained by the rheological assays. This figure shows that the shear stress depends linearly on the shear rate, for all the studied PILs.

The viscosity of PILs depends on their molecular characteristics, the form of cations and anions and their packing and orientation into the bulk fluid.<sup>57,58</sup> Figure 5 shows the viscosity–shear rate curves at 298.15 K for the three less viscous PILs. As occurs for all the studied PILs, it can be found that they gather a non-Newtonian profile in a specific range of shear rate ( $<30 s^{-1}$ ).<sup>43,58–60</sup> At low shear rates, all the studied PILs show shear-thinning behavior (the viscosity decreases with the shear rate increase), except for 2-HEAPr, 2-HDEAOx, and 2-HDEASu, which show a shear-thickening behavior, known as dilatant fluids. However, for practical purposes, once the agitation increases it induces a disruption in the ionic interactions that support the crystalline structure, reducing the non-Newtonian behavior at sufficiently high shear rates ( $>30 s^{-1}$ ).<sup>43,60</sup>

**Color Measurements.** The cotton fabrics were evaluated for their color strength and color appearance indicated by the  $K/S$  and  $L^*a^*b^*$  values, taken at the peak wavelength, 490 nm. Figure 6 gathers the  $K/S$  values for dyed samples washed into cool and hot washing bath at conditions previously indicated. The dyed cotton fabrics into water, then washed into a cool bath, exhibited a higher  $K/S$  value than its pair, washed into a hot bath. In general, this fact should be too observed for the other samples, dyed into ionic medium (PIL + reactive dye), since higher temperatures increase the solubility of the reactive dye into washing water, and the unfixed dye is easier removed from the samples in the fiber surface. A possible explanation for some exceptions, for example, samples dyed into 2-HEAA, 2-HDEASa, and 2-HDEAPr, which show highest effectiveness when hot washed, is the probable higher capability of these PILs to change the cellulose structure, promoting a better dye insertion on the fiber. In these cases, the hot water of washing does not remove the unfixed dyestuff but increases its fixation, once it is embedded into the structure and not in the fiber surface. The cool washed fabrics dyed into 2-HEAPr, 2-HEAA, and 2-HEACi, and the hot washed fabrics dyed into 2-



**Figure 6.**  $K/S$  values for the cool-washed and hot-washed cotton fibers. Dashed lines are the reference  $K/S$  values for the blank (fabric dyed into aqueous medium).

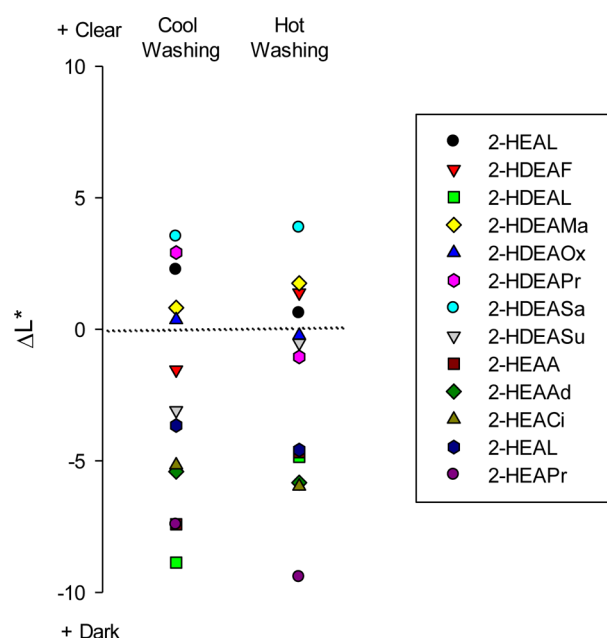


**Figure 7.** CIE  $L^*a^*b^*$  space color for the (a) cool-washed and (b) hot-washed cotton fibers. The axis  $-a^*$  to  $+a^*$  represents the opponent colors of green and red, respectively, and the axis  $-b^*$  to  $+b^*$  represents the opponent colors blue and yellow, respectively.

HEAAd, 2-HEAPr, 2-HEAA, 2-HEACi, 2-HDEAPr, and 2-HDEAA exhibited higher  $K/S$  values than that dyed into water being washed at the same conditions, which expresses the efficiency of these PILs as dyeing vectors and also their higher capability as dye fixatives, when compared to water.

In terms of perceptual color, the dyeing quality could be better evaluated by analyzing the CIE  $L^*a^*b^*$  color space. Figure 7a and b gathers the  $a^*$  and  $b^*$  color coordinates for the dyed samples washed in cool and hot baths, respectively. These graphics are a traditional two-dimensional CIE  $L^*a^*b^*$  color space plot, where the abscissa varies from  $-a^*$  (at the left) to  $+a^*$  (at the right), showing the opponent process colors (green and red, respectively). On the other hand, the ordinate shows from  $-b^*$  (at the bottom) to  $+b^*$  (at the top), representing the opponent colors blue and yellow, respectively. When compared with the aqueous-dyed blank, the cool-washed samples dyed

into 2-HEAA, 2-HEACi, 2-HDEAL, 2-HEAL, 2-HEAPr, 2-HEAAd, 2-HDEASu, and 2-HDEAOx exhibited a more blue (more negative  $b^*$ ) and less red (more negative  $a^*$ ) appearance, except 2-HDEAOx, with no significant changes in the green–red axis, and 2-HEAAd and 2-HEAPr, with a slightly red perceptual color (more positive  $a^*$ ). For the hot-washed samples, almost all the tested PILs produced a sample with a more blue appearance than that dyed into water, in the following order: 2-HDEAL, 2-HEAAd, 2-HEAPr, 2-HEAL, 2-HEAA, 2-HDEAMa, 2-HDEAOx, 2-HDEASu, 2-HDEAPr, and 2-HDEAA. From this collection, only the samples dyed into 2-HEAPr, 2-HEAAd, and 2-HEACi exhibited an additional slightly red appearance. Low  $K/S$  values, but higher blue appearance if compared with the black sample (as samples dyed into 2-HEAL and 2-HDEAOx) should be justified by the differences in lightness and darkness ( $\Delta L^* = L^* \text{ sample minus}$

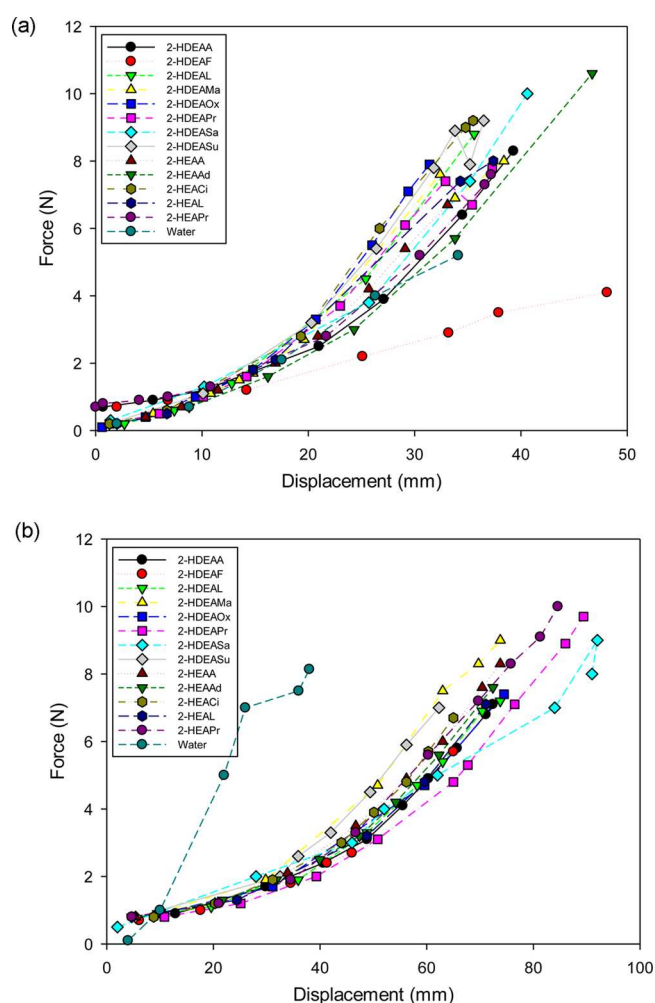


**Figure 8.** Differences in lightness and darkness ( $\Delta L^* = L^*$  sample minus  $L^*$  blank) of the cool-washed and hot-washed samples.

**Table 1. Tensile Properties (ASTM D5035-95) of Cool-Washed and Hot-Washed Cotton Samples**

protic ionic liquid	force in the maximum peak (N)	displacement (mm)	elongation %
Cool-Washed Samples			
2-HDEAA	8.34	46.04	153.47
2-HDEAF	4.12	52.87	176.23
2-HDEAL	8.83	44.38	147.93
2-HDEAMa	8.04	41.09	136.97
2-HDEAOx	7.95	41.56	138.53
2-HDEAPr	7.85	39.17	130.57
2-HDEASa	10.40	50.11	167.03
2-HDEASu	9.22	46.04	153.47
2-HEAA	6.67	42.87	142.90
2-HEAAd	10.59	50.73	169.10
2-HEACi	9.22	46.98	156.60
2-HEAL	8.04	47.86	159.53
2-HEAPr	7.55	43.33	144.43
water	5.79	47.70	158.00
Hot-Washed Samples			
2-HDEAA	8.04	81.98	163.96
2-HDEAF	5.79	78.60	157.20
2-HDEAL	7.16	76.56	153.12
2-HDEAMa	9.22	88.70	177.40
2-HDEAOx	7.46	98.91	329.70
2-HDEAPr	9.71	98.91	197.82
2-HDEASa	8.83	94.12	188.24
2-HDEASu	7.26	79.22	158.44
2-HEAA	8.73	91.46	182.92
2-HEAAd	7.95	86.04	172.08
2-HEACi	7.06	81.30	162.60
2-HEAL	7.06	98.91	197.82
2-HEAPr	10.01	88.70	177.40
water	8.14	60.31	201.03

$L^*$  standard; Figure 8). These samples exhibited a more blue color, but a brighter appearance (far of black and next of white



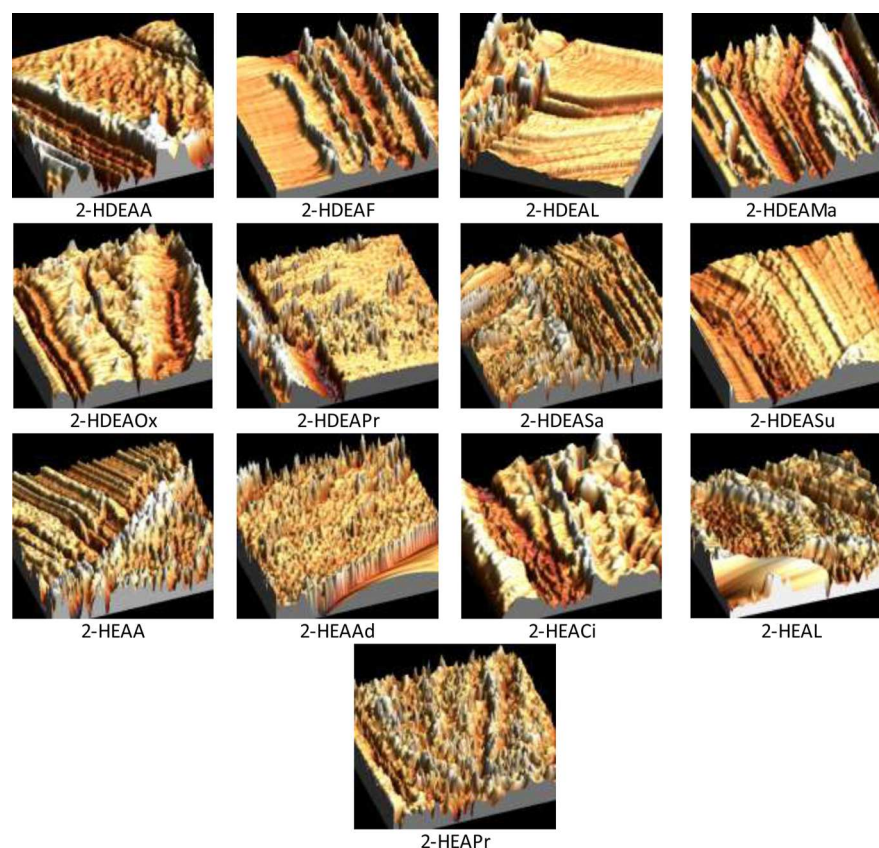
**Figure 9.** Tensile stress–elongation curves of the (a) cool-washed and (b) hot-washed cotton samples.

in the color space), which results in an increased reflectance and decreasing their  $K/S$  value.

**Mechanical Properties of Samples.** The strength of a textile depends on the strength of the constituent yarn and on the fabric geometry. Tensile properties (force in the maximum peak, displacement, and elongation; see Table 1), measured following the ASTM D5035-95 method, show that these mechanical properties are slightly modified as a consequence of cotton dyeing into a different media and washing at different temperatures.

The largest increase in tearing strength was observed for the hot-washed samples dyed into 2-HDEAA (Figure 9a) and cool-washed sample dyed into 2-HEAAd (Figure 9b). A small difference in tearing strength (in terms of both tensile strength and percent elongation) after cotton dyeing into aqueous and ionic medium is possibly due to the PIL increasing the warp and weft slippage, resulting in a more efficient redistribution of force concentrations throughout the textile structure.

**Surface Morphology of Samples.** AFM measurements were used to analyze the PILs influence in the tissue surface after dyeing. Figure 10 shows the 3D images obtained by AFM of the fabrics treated with the different PILs. All samples presented distinct roughness characteristics. The roughness is a factor that can influence the cleanability and comfort of the



**Figure 10.** AFM height images of the cotton fibers dyed into 2-HDEAA, 2-HDEAF, 2-HDEAL, 2-HDEAMa, 2-HDEAOx, 2-HDEAPr, 2-HDEASa, 2-HDEASu, 2-HEAA, 2-HEAAd, 2-HEACi, 2-HEAL and 2-HEAPr.

**Table 2.** Maximum Surface Roughness (nm) and Average Roughness (nm) of Fabrics Treated with Different Protic Ionic Liquids

protic ionic liquids	maximum surface roughness (nm)	average roughness (nm)
2-HDEAA	115.88	25.16
2-HDEAF	218.61	37.37
2-HDEAL	84.91	17.11
2-HDEAMa	285.37	68.34
2-HDEAOx	48.40	9.49
2-HDEAPr	90.35	19.33
2-HDEASa	333.46	70.86
2-HDEASu	245.76	37.60
2-HEAA	152.40	32.10
2-HEAAd	70.39	13.15
2-HEACi	169.34	36.97
2-HEAL	104.50	20.47
2-HEAPr	63.39	13.31

fabrics. Table 2 shows the values of maximum roughness and average roughness of all images of Figure 10.

Fabrics treated with the PILs 2-HDEAMa, 2-HDEASu, 2-HDEASa, and 2-HDEAF showed the highest values of maximum roughness ( $\geq 200$  nm), fabrics treated with 2-HEAL, 2-HEAA, 2-HDEAA, and 2-HEACi presented intermediate values (100–200 nm), while fabrics treated with 2-HDEAL, 2-HDEAPr, 2-HEAPr, 2-HEAAd, and 2-HDEAOx showed the lowest values ( $\leq 100$  nm).

Considering the values gathered in Table 2, the average roughness for all fabrics is less than 72 nm, and the fabrics

exposed to 2-HEAPr, 2-HEAAd, and 2-HDEAOx showed the lowest values ( $< 15$  nm). In accordance to the average roughness values, the PILs 2-HEAPr, 2-HEAAd, and 2-HDEAOx should be the most suitable dyeing media for textile processes, since they produced a decrease in the roughness of the fabric and as a consequence these will offer a smaller area of contact, decreasing adherence of impurities, and less friction with the skin, resulting in greater comfort for the consumer.

## CONCLUSIONS

There are many factors that influence fabric dyeing quality, and these results clearly show that PIL structure affects the cotton fiber as well as the dyeing process.

As discussed in the scientific literature, the chemical reactions with cotton cellulose occur mainly due to the activity of hydroxyl groups. The reactions occur in the more accessible amorphous regions and at the surfaces of crystalline regions, and are divided into two categories: esterification, that carried out under acidic medium, and etherification, that which occurs in an alkaline medium. Under these alkaline conditions, cellulose behaves as a weak acid and reacts with reactive dyes by nucleophilic substitution or addition. The evidence for reactive dyes forming a covalent bond with the cellulose anion (cellulose- $O^-$ ) was previously gathered.<sup>61</sup> For these reasons, in general terms, the alkaline PILs (2-HEACi (pH 9.30), 2-HEAAd (pH 9.09), 2-HEAA (pH 8.80), 2-HDEAA (pH 8.58), 2-HEAPr (pH 8.36), and 2-HDEAPr (pH 8.27)) showed better results in terms of dyeing quality ( $K/S$ ) than the acidic PILs (2-HDEASu (pH 7.49), 2-HDEAMa (pH 7.25), 2-



HDEASa (pH 7.00), 2-HEAL (pH 6.95), 2-HDEAF (pH 6.19), 2-HDEAL (pH 5.07), and 2-HDEAOx (pH 4.96)).

Similarly, the PIL structure (ionic chains) seems to influence dyeing quality. As previously discussed, the organic residual chain in the ions has strong effects on their thermodynamic properties, the steric hindrance being an important factor for accommodation into a liquid net and, thus, access to active points of the cellulose fiber structure.

Among many structural factors, such as chain length of anion and the bulk character of substitution and the degree of substitution of the cation, the latter seems to be the more significant. PILs formed by monosubstituted amines (2-HEAPr, 2-HEAA<sub>d</sub>, 2-HEAC<sub>i</sub>, 2-HEAA, 2-HEAC<sub>i</sub>, and 2-HEAL, in this order) showed better results in terms of dyeing quality (K/S) than those formed by disubstituted amines.

The diffusion of the constituent ions into the fiber pores<sup>30</sup> and the probable capability of the IL anion to interact with cellulose<sup>62,63</sup> reduce the degree of crystallinity, producing a swelling effect and increasing the dye diffusion into the fiber, partially diminishing the need for auxiliary chemicals (mordants, dispersants, swelling and wetting agents, etc.) and, then, reducing the concentration and amount of potential pollutants. These traditional auxiliary agents require large water amounts to eliminate them from the fabrics and usually remain in dyebaths, contributing to the organic load of wastewater. On the other hand, PILs can be easily removed from the fabrics since they are infinitely soluble in water,<sup>39,41,42</sup> a real advantage of the PILs when compared to aprotic ionic liquids (AILs) which show low solubility in aqueous media. Reduction of water consumption is one of the principal targets to improve the sustainability of cotton dyeing processes; additionally, the proposed system allows the recycling of the PIL, since after dyeing, the unfixed dye remains in the bath, and it can be reused until complete consumption, providing environmental and economic benefits.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.7b01555](https://doi.org/10.1021/acssuschemeng.7b01555).

Detailed spectroscopic and thermodynamic characterization of the studied protic ionic liquids (PDF)

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### Notes

The authors declare no competing financial interest.

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