

# Influence of Acetated-Based and Bromo-Based Ionic Liquids Treatment on Wool Dyeing with Acid Blue 7

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**ABSTRACT:** Bromo-based and acetated-based ionic liquids (ILs), 1-butyle-3-methylimidazolium bromo ([Bmim]Br), 1-ethyl-3-methylimidazolium bromo ([Emim]Br), 1-butyle-3-methylimidazolium acetate ([Bmim]Ac), and 1-ethyl-3-methylimidazolium acetate ([Emim]Ac), were synthesized and employed for wool surface treatment. Scanning electron microscope results indicated that the wool surfaces treated with acetated-based ILs were eroded more than those treated with bromo-based ILs. Comparable studies showed that the wool samples treated with acetate-based ILs, especially [Emim]Ac, had higher initial dyeing rate and equilibrium exhaustion than those with bromo-based ILs. Along with treatment temperature and time increasing, acetate-based ILs had more remarkable effects on mechanical and

dyeing properties of the wool samples than bromo-based ILs. The wool samples treated with [Emim]Ac at 60°C for 10 min had excellent low-temperature dyeing properties. The color depth (K/S) investigations showed that the wool samples treated with acetate-based ILs possessed darker color depth than those treated with the bromo-based ILs. Color fastnesses of the wool samples treated with [Bmim]Br, [Emim]Br and [Bmim]Ac exhibited the same grades as the untreated sample, while wet color fastnesses of [Emim]Ac treated sample were slightly decreased. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3283–3291, 2012

**Key words:** ionic liquids; wool; modification; dyeing; equilibrium exhaustion; substantivity

## INTRODUCTION

Wool is the most important animal fiber used in the textile industry, and it has a complex physical and chemical structure.<sup>1</sup> In the chemical structure, wool is basically made up of cuticle, cell membrane complex, and cortex.<sup>2,3</sup> A cuticle (flattened cells) is made up of an outmost scale layer and a thin outer layer (epicuticle).<sup>2</sup> The two layers are hydrophobic, which results in considerable resistance to dye adsorption and penetration from the surface layer to the interior of wool fiber.<sup>4</sup> Additionally, the cuticles on wool surface produce undesired felting.<sup>5</sup> To improve dyeability and reduce felting of wool, modification of cuticles on the wool surface is urgently required.

Conventional modifications of wool are involved with chloration and oxidation in which a large

amount of chemicals from incomplete reactions pollute the effluent.<sup>6,7</sup> Owing to the increasing awareness of ecological and economical restrictions imposed on the textile industry, there are many alternative wool modifications such as low temperature plasma<sup>1,8–11</sup> and corona irradiations,<sup>12–14</sup> liquid ammonia treatment,<sup>9,15</sup> and protease hydrolysis.<sup>4,16,17</sup> However, the low temperature plasma and corona modifications have serious obstacles such as costs, compatibility and capacity, which greatly restrict their application in the textile industry. Furthermore, they would generate a rather harsh handle.<sup>11–14</sup> In terms of liquid ammonia treatment, the high pressure and low temperature of operating conditions curb its application in the textile processing. Protease treatment can replace harsh chemicals, which process is mild and biodegradable. But due to strongly chemical inertia of the cuticle, it is difficult for protease to attack and hydrolyze it. Therefore, pretreatment using chemicals is required before protease treatment.<sup>14,17</sup>

Ionic liquids (ILs) are low-melting salts (melting point < 100°C) forming liquids that consist only of cations and anions.<sup>18</sup> Due to their characteristics such as nonvolatility, nonflammability, thermal stability, high solubility, noncontamination, and ease of recycling, ILs have recently received much attention

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as green solvents and very promising replacements for the traditional volatile organic solvents.<sup>19,20</sup> So far, ILs have been applied in dissolving, regenerating,<sup>21–26</sup> and modifying natural fibers.<sup>27,28</sup>

Recently, Yuan et al.<sup>28,29</sup> have investigated dyeing properties of wool fiber treated with [Bmim]Cl at various temperatures (80, 100, or 120°C) and found that hydrophilicity and dyeing rate of treated wool were significantly increased because the scales of wool fiber surface were partly eroded by [Bmim]Cl. It is clear that the application of ILs for wool modification is a new and feasible, simple, and eco-friendly method. In fact, IL consists of 100% cation and anion, which govern melt point, viscosity, and dissolving properties for organic and inorganic compounds and polymers.<sup>30,31</sup> It is valuable to investigate influences of cation and anion of IL on wool physical and chemical properties.

In this work, four ILs ([Bmim]Br, [Emim]Br, [Bmim]Ac, [Emim]Ac) were synthesized and used for modification of wool. The surface morphologies of treated samples using the four ILs were investigated, and the mechanical properties, dyeing properties, color depth (K/S), and color fastnesses of IL treatment wool samples were evaluated systematically.

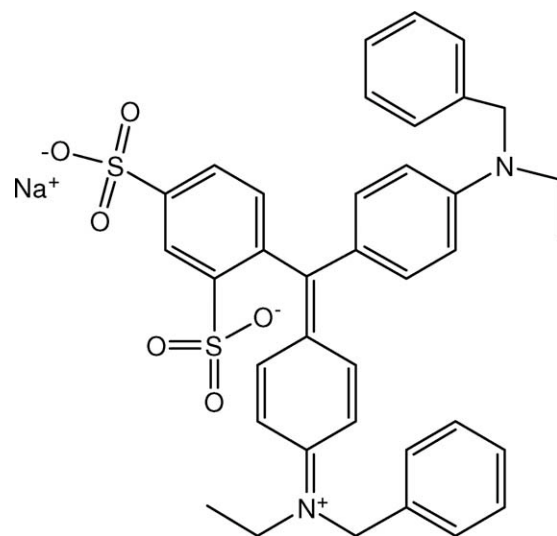
## EXPERIMENTAL

### Chemicals and materials

All the chemicals used were of analytical grade and commercially available unless otherwise mentioned. 2/14 Nm 100% Wool yarns (average diameter of fibers is about 27.3  $\mu\text{m}$ ) were kindly supplied by Tongxiang Xingguang Wool Mill (China). Before using, not all yarn samples were pretreated further. For wool dyeing, we selected Acid Blue 7 (C.I. 42080; commercial grade; Tianjin Tianshun Chemical Dye-stuff, China) for its wide use in various industries like cloth, leather, soap industry etc., for dyeing purpose. As shown in Scheme 1, Acid blue 7 is a triaryl-methane dye and has a remarkably bright and strong color. It has threefold hydrophilic groups, two sulfonated groups and one quaternary ammonium group, and is a rather hydrophilic dye. It was chosen to mark the contrast in the dyeing of untreated and IL-treated wool without further purification.

### Measurements

Infrared spectra were registered on Thermo Fisher Nicolet Avater 370 FTIR spectrophotometer. <sup>1</sup>H-NMR (400 MHz) was recorded on a Bruker AM-400 spectrometer with Me<sub>4</sub>Si as internal standard. Differential scanning calorimetry (DSC) was conducted on a NetZSch (German) DSC 200F3 system under nitrogen to obtain the melt points. Initial sample



Scheme 1 Molecular structure of Acid Blue 7.

weight was set as 1–2 mg for each operation. The specimen was cooled from 25 to  $-60^{\circ}\text{C}$  at a cooling rate of  $5^{\circ}\text{C}/\text{min}$  and then heated from  $-60$  to  $150^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The surface morphologies of wool fibers were visualized using a JSM-6360LV Scanning Electron Microscope (SEM). The samples were positioned and gold-sputtered under vacuum before observation. The wool damage (alkali solubility, %) due to ILs treatment was determined according to ISO 3072 1975(E).

### IL synthesis

#### [Bmim]Br

The IL of [Bmim]Br was synthesized in the laboratory using reported procedure.<sup>30</sup> In a typical preparation, 54.82 g (0.40 mol) bromobutane and 32.8 g (0.40 mol) 1-methylimidazole were added to a round-bottomed flask fitted with a reflux condenser for 24 h at  $80^{\circ}\text{C}$  with stirring. The top phase of the two phases formed contains starting material, which can be removed by washing twice with ethyl acetate. This also ensures the removal of the unreacted material in the bottom phase containing IL product. The yellowish IL product of [Bmim]Br was further heated to  $50^{\circ}\text{C}$  on a rotary evaporator to eliminate any dissolved ethyl acetate solvent. M.p.  $66\text{--}68^{\circ}\text{C}$ . IR, (KBr)  $\nu$ ,  $\text{cm}^{-1}$ : 3423.78 (hydrogen bond of Br<sup>-</sup>H or O<sup>-</sup>H), 3148.78, 3098.63 (aromatic C–H vibrations), 2961.89, 2872.81 [(CH<sub>2</sub>)<sub>n</sub>-CH<sub>3</sub> vibrations] 1569.59, 1463.39 (symmetric vibrations of aromatic ring), 1168.27 (symmetric vibrations of aromatic ring), 917.47, 754.01 (bending vibrations of aromatic C–H). <sup>1</sup>HNMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ , ppm: 9.40 (s, 1H), 7.87 (t, 1H), 7.74 (t, 1H), 4.18 (q, 2H), 3.88 (s, 3H), 1.80 (m, 2H), 1.34 (m, 2H), and 0.91 (t, 3H).

**[Emim]Br**

Equal molar amounts of bromoethane and 1-methylimidazole were synthesized to obtain "[Emim]Br" with the same method as "[Bmim]Br." M.p. 60–62°C. IR, (KBr)  $\nu$ ,  $\text{cm}^{-1}$ : 3425.27 (hydrogen bond of Br $\cdots$ H or O $\cdots$ H), 3152.61, 3102.09 (aromatic C–H vibrations), 2964.12, 2876.71 [(CH<sub>2</sub>)<sub>n</sub>–CH<sub>3</sub> vibrations], 1633.52, 1459.13 (symmetric vibrations of aromatic ring), 1169.37 (symmetric vibrations of aromatic ring), 1086.39, 754.67 (bending vibrations of aromatic C–H). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ , ppm: 9.98 (s, 1H), 7.83 (t, 1H), 7.74 (t, 1H), 4.2 (q, 2H), 3.87 (s, 3H), and 1.40 (t, 3H).

**[Bmim]Ac**

According to Ref., 32 the acetic-based IL of "[Bmim]Ac" is prepared through the ion exchange reaction. In a typical procedure, 19.61 g (0.2 mol) dried potassium acetate was completely dissolved in 120 mL, then 43.81 g (0.2 mol) "[Bmim]Br" was slowly added to the above solution with stirring. Suddenly white precipitation (potassium bromide) was produced due to the fact that the solubility of potassium bromide in ethanol is very low. The reaction system was set at 40°C for 5 h with stirring, subsequently placed at 0°C water bath for 1 h. Keeping cool, reaction mixture was quickly filtered off. The ethanol was separated from the filtrate on a rotary evaporator to give crude product. The crude product was placed at 0°C for overnight and filtered to remove the precipitation. The resulting IL was pale yellow liquid at room temperature. M.p. no clear melting peak. IR, (KBr)  $\nu$ ,  $\text{cm}^{-1}$ : 3420.86 (hydrogen bond of O $\cdots$ H), 3148.61, 3096.09 (aromatic C–H vibrations), 2965.64, 2875.44 [(CH<sub>2</sub>)<sub>n</sub>–CH<sub>3</sub> vibrations], 1643.35, 1458.03 (symmetric vibrations of aromatic ring), 1567.11, 1407.53 (symmetric vibrations of C=O), 1168.91 (symmetric vibrations of aromatic ring), 1067.62, 1017.62, 651.99 (bending vibrations of aromatic C–H). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ , ppm: 10.02 (s, 1H), 7.86 (t, 1H), 7.75 (t, 1H), 4.19 (q, 2H), 3.87 (s, 3H), 1.81 (m, 2H), 1.59 (s, 3H), 1.32 (m, 2H), and 0.93 (t, 3H).

**[Emim]Ac**

The preparation of [Emim]Ac was similar to that of [Bmim]Ac. The resulting product was pale yellow liquid at room temperature. M.p. no clear melting peak. IR, (KBr)  $\nu$ ,  $\text{cm}^{-1}$ : 33417.07 (hydrogen bond of O $\cdots$ H), 3149.11, 3097.18 (aromatic C–H vibrations), 2966.28, 2872.56 [(CH<sub>2</sub>)<sub>n</sub>–CH<sub>3</sub> vibrations], 1645.52, 1459.53 (symmetric vibrations of aromatic ring), 1567.11, 1406.68 (symmetric vibrations of C=O), 1170.34 (symmetric vibrations of aromatic ring),

1085.89, 1017.43, 649.19 (bending vibrations of aromatic C–H). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ , ppm: 10.01 (s, 1H), 7.85 (t, 1H), 7.75 (t, 1H), 4.21 (q, 2H), 3.86 (s, 3H), 1.54 (s, 3H), and 1.39 (t, 3H).

**Ionic liquid treatment**

The wool yarn sample was separately treated using synthesized four ILs in 250 mL-conical flasks at different temperature (60 or 80°C) for 10 or 20 min with stirring, and the liquor-to-goods ratio for ionic liquid treatment was 30 : 1. Then wool samples were squeezed to remove the absorbed IL as far as possible and subsequently washed three cycles with ethanol at room temperature. Finally, wool samples were rinsed twice with deionized water and dried at 80°C.

**Tensile strength test**

The tensile strength of wool fiber yarns was determined using an auto single yarn strength tester YG029C (Ningbo Textile Instrument Factory, China) according to ISO 2062 : 1995. Testing condition is as follows: gauge length is 250 mm, rate displacement is 500 mm/min, and pretension: 0.5 CN/tex. The samples were balanced at 25°C and RH 60% for 24 h before testing. The results were given as the arithmetic means of 10 different times.

**Dyeing**

The dyeing of wool yarns was carried out in an oscillating dyeing machine (Honsun Machine, Foshan, China). Wool samples were dyed with 4% (o. w. f) Acid Blue 7 at a setting temperature (70, 80, 90, or 100°C) for 120 min with a liquid-to-goods ratio of 100 : 1. The dyeing system was maintained at pH 4–5 with acetate acid. The dyeing concentration in the dyebath was determined by measuring the absorbance at  $\lambda_{\text{max}}$  (640 nm) in a 1 cm quartz absorption cell using a UV-vis Spectrophotometer. All measurements of the dye solution were conducted at room temperature and the percentage exhaustion was calculated according to the following eq. (1).

$$E = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\% \quad (1)$$

where  $E$  is the percentage exhaustion at time  $t$ ,  $A_0$  is the initial absorbance of dye bath at 0 min,  $A_t$  is the absorbance of the dye bath at time  $t$ .

**Substantivity**

The substantivity,  $K$ , which represents a measure of the extent to which dye prefers the fiber to the dye

bath in particular dye bath conditions, was calculated by eq. (2).<sup>1</sup>

$$K = \frac{E \times L}{100 - E} \quad (2)$$

where  $E$  is the percentage exhaustion at equilibrium,  $L$  is the liquor ratio.

### Color depth

The colorimeter data of colored wool yarns was measured on a Color-Eye 7000A spectrophotometer interfaced to a computer with the measuring condition of D65/10° and SAV. The color depth ( $K/S$ ) of the dyed samples was evaluated by light reflectance technique and the  $K/S$  values were assessed using the Kubelka-Munk eq. (3).

$$K/S = (1 - R)^2/2R \quad (3)$$

where  $R$  is the reflectance,  $K$  is the absorption coefficient, and  $S$  is the light-scattering coefficient.

### Colorfastness measurement

Color fastnesses were tested according to ISO 105-C01 : 1989 (Color fastness to water washing) and ISO 105-X12 : 2001 (color fastness to rubbing).

## RESULTS AND DISCUSSION

### Surface morphology

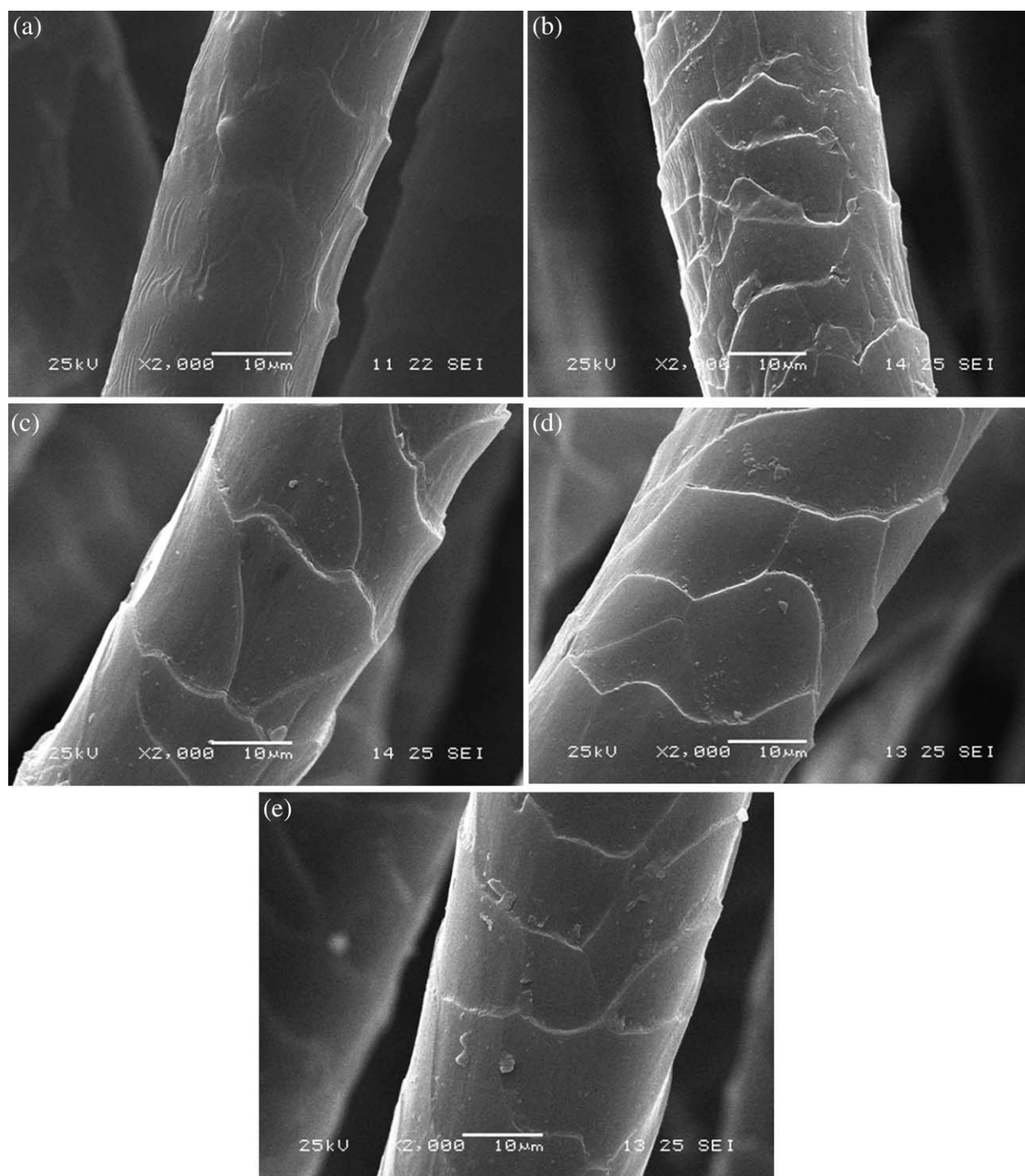
In the surface morphology structure, wool is characterized by the cuticles, which play a critical role in adsorption and diffusion of dyes during dyeing. The surface micrographs of wool fibers treated with different IL at 60°C for 10 min are shown in Figure 1. It can be seen from Figure 1(a) that the scales of the untreated wool are blurred but shapes of cuticles overlapping one another are sharp. This is different from the results obtained by Kan<sup>10</sup> and Yuan.<sup>28</sup> The reason is that the wool scouring in our experiments was not carried out, and thus intact cuticles are coated by a layer of impurities including wool grease and perspiration, spinning lubricant agents, dusts in storage, and so on. In fact, it is easy to remove the layer of impurities by aqueous or solvent scouring while it is difficult for cuticles of wool surface to remove simply by the scouring. Generally, cuticles consist of epicuticle, exocuticle, endocuticle, and intercellular cement.<sup>3</sup> The outmost exocuticle, which contains a high number of disulphide cystine crosslinkages, is responsible for the well chemical inertia to most of alkali, acid, reductant, oxidant, and protease.<sup>3</sup> Thus, the cuticles make wool surface

hydrophobic and thus hinder the surface adsorption and internal diffusion of dyes such as acid dyes, direct dyes, and reactive dyes.

The SEM micrographs of wool samples [Fig. 1(b–e)] treated by the four IL at 60°C reveal deterioration of the cuticles compared with the untreated sample [Fig. 1(a)]. For the [Bmim]Br treated sample, as shown in Figure 1(b), it can be seen that tips and edges of cuticles are slightly destroyed except for some impurities in the groove of cuticles. From Figure 1(c), it is clear that impurities on the fiber surface are invisible, and cuticle tips and edges are mostly removed. In Figure 1(d), it can be found that part of cuticles is in some degree dissolved and the wool fiber becomes round and smooth. As more cuticles are stripped, the fiber Figure 1(e) becomes rounder and smoother than that in Figure 1(d). In terms of the effect of modification, there is an increasing order of [Bmim]Br < [Emim]Br < [Bmim]Ac < [Emim]Ac. It can be concluded that the acetate-based ILs have a stronger modification effect on the wool fiber than the bromo-based ILs, which can be attributed to acetate-based ILs with lower melt point (<−20°C)<sup>31,33</sup> and viscosity (<18 cp at 25°C).<sup>34</sup> Melting point of ILs is an important property related to their application temperatures. DSC determination showed that melting points of [Bmim]Br and [Emim]Br were 66–68°C and 60–62°C, respectively. However, melting points of [Bmim]Ac and [Emim]Ac could not be obtained by DSC, which is probably due to the fact that [Bmim]Ac and [Emim]Ac are generally liquid up to −30 to −50°C and become increasingly viscous, turning finally into glasses without the observation of a melting point.<sup>35</sup> Alkali solubility was used to evaluate the wool fiber damage after ILs treatment.<sup>36</sup> The alkali solubilities of wool samples untreated, treated with [Bmim]Br, and treated with [Bmim]Ac are 6.6, 6.8, and 7.3%, respectively. It shows ILs treatment can bring some damage to the pristine wool fiber. The more damage of the wool treated with acetate-based ILs was occurred due to their better solubility, compared with bromo-based ILs. Therefore, under the same treatment temperature, the acetate-based ILs can more easily attach to the wool cuticle, swell and eventually dissolve it out by disrupting hydrogen bonds<sup>22,24,37</sup> and intermolecular bonding (disulphide linkages) of the cuticle layer.

### Mechanical properties

Mechanical properties of wool yarns are important, which determine the post processes and wear performance. The results presented in Table I show that the tensile strength values decrease after IL treatment while elongation at break percentages increase. The strength decreasing effect can be probably



**Figure 1** SEM of wool fibers after treatment at 60°C for 10 min with different IL (a: untreated; b: [Bmin]Br; c: [Emim]Br; d: [Bmin]AC; e: [Emin]AC).

attributed to the disruption of hydrogen bonds and disulphide linkages and the partial cleavage of the cuticles by IL treatment. The cleavage of the cuticles makes the wool surface rounder and smoother, which leads to the decrease in the interfiber frictional force. Hence, fewer forces are required to overcome the interfiber friction before the occurrence of yarn breakage, resulting in a lower breaking

load.<sup>38</sup> However, the removal of the cuticles can facilitate ILS to penetrate into the interior of the fiber and partly degrade the cortical cells, which results in the mechanical decrease of the fiber. The increase of the elongation at break percentages is probably due to the partial cleavage of the hydrogen bonds and disulphide linkages in the cuticle. This cleavage could soften the wool scales, thus making the fibers

TABLE I  
Dyeing Kinetics Parameters and Tensile Properties of the Wool Samples

ILs	Treating conditions	$t_{1/2}$ (min)	$E$ at $E_m$ (%E)	Liquor ratio (L)	Substantivity (K)	Elongation at break (%)	Tensile strength (CN)
[Bmim]Br	Untreated	17.92	77.9	100	352.49	17.2	301
	60°C, 10 min	15.24	81.43	100	438.50	21.8	288 (95.7%)
	60°C, 20 min	11.95	83.79	100	516.90	27.3	268 (89%)
	80°C, 10 min	13.82	86.01	100	614.80	30.1	252 (83.72%)
[Emim]Br	80°C, 20 min	13.39	88.53	100	771.84	32.9	231 (76.7%)
	60°C, 10 min	10.9	84.05	100	526.96	23.5	270 (89.7%)
	60°C, 20 min	9.67	85.26	100	578.43	28.4	248 (82.39%)
	80°C, 10 min	8.01	90.51	100	953.74	30.6	245 (81.4%)
[Bmim]Ac	80°C, 20 min	7.59	93.08	100	1345.09	32.9	225 (74.8%)
	60°C, 10 min	5.09	87.15	100	678.21	32.1	261 (86.7%)
	60°C, 20 min	—	—	—	—	—	—
	80°C, 10 min	5.11	95.25	100	2005.26	33.2	218 (72.4%)
[Emim]Ac	80°C, 20 min	—	—	—	—	—	—
	60°C, 10 min	3.85	95.84	100	2303.85	32.8	241 (80.7%)
	60°C, 20 min	—	—	—	—	—	—
	80°C, 10 min	—	—	—	—	—	—
	80°C, 20 min	—	—	—	—	—	—

Note: The sign, —, indicates fiber was dissolved when treatment; the values in the bracket show strength retention compared with the untreated sample.

more elastic. In addition, the increase in interfiber frictional force could further enhance this effect. It is noteworthy that comparing the effect of various ILs on tensile strength and elongation at break, an increasing order is [Bmim]Br < [Emim]Br < [Bmim]Ac < [Emim]Ac. Raising temperature or elongating time, a remarkable decrease in tensile strength happened to all treated samples, especially to the samples treated with the acetated ILs. These results are ascribed to the more solubility of acetate-based ILs than that of bromo-based ILs. To obtain good extensibility and less tensile strength loss of wool yarns, it is required to choose the suitable ILs and treatment conditions.

#### Effect of ILs treatment on dyeing of wool fiber yarns

The exhaustion curves of IL-treated and untreated samples dyeing at 80°C are shown in Figure 2, while Table I lists the results of time of half dyeing ( $t_{1/2}$ ), percentage of exhaustion at equilibrium ( $E$  at  $E_m$ ) and substantivity ( $K$ ) obtained from Figure 2. From Figure 2, it is clear that there are two stages during dyeing wool fibers with acid dyes, which are the adsorption and diffusion of dyes to the fiber (the initial dyeing stage) and the dispersion and immobilization of dyes within the fiber (the equilibrium exhaustion stage),<sup>7,39</sup> respectively.

First, it can clearly seen that the slopes of all the curves representing IL-treated samples at the start of dyeing are steeper than that of the untreated sample (Fig. 2), which indicates that the IL-treated wool samples have better adsorption abilities than the

untreated sample. To quantify the dyeing rate in a dyeing system of textiles, the half-dyeing time ( $t_{1/2}$ ) is introduced, which refers to the time taken to adsorb 50% of the dyes amount at equilibrium. From Table I,  $t_{1/2}$  values of all samples decrease in the order of untreated (17.92 min) > [Bmim]Br (15.24 min) > [Emim]Br (10.9 min) > [Bmim]Ac (5.09 min) > [Emim]Ac (3.85 min). Second, equilibrium exhaustion of untreated wool sample only attain 77.9% while equilibrium exhaustion values of IL-treated samples increase in the order of [Bmim]Br (81.43%) < [Emim]Br (84.05%) < [Bmim]Ac (87.15%) < [Emim]Ac (95.84%). To characterize how efficiently dye molecules have been transferred from the bath to the fiber,  $K$  is used, which represents the

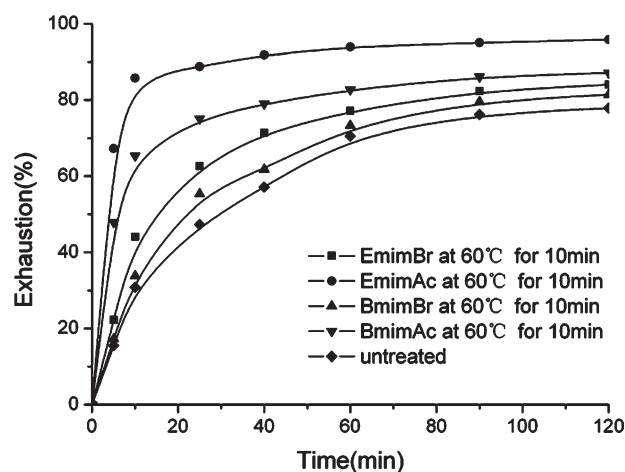
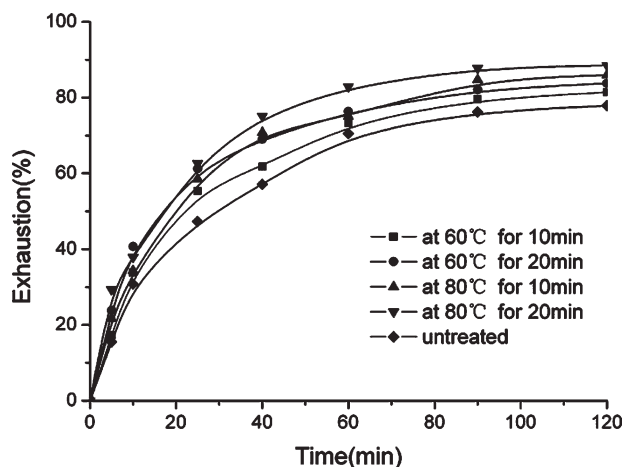
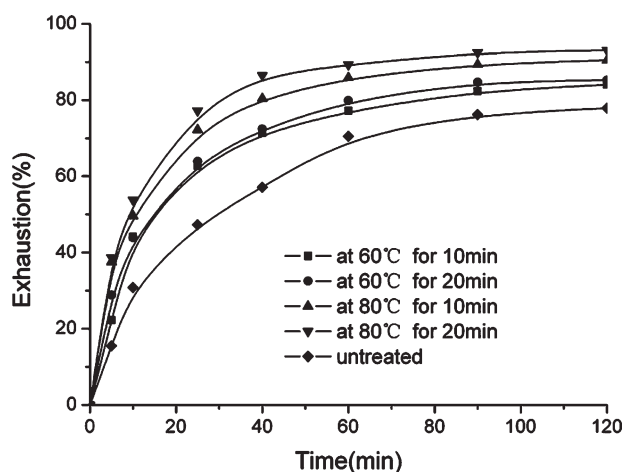


Figure 2 Exhaustion versus time among untreated and IL treated wool samples dyeing at 80°C.

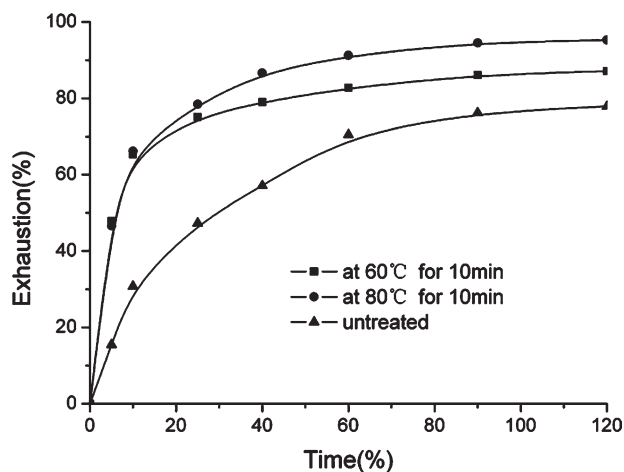


**Figure 3** Exhaustion versus time for dyeing of wool fibers with [Bmim]Br dyeing at 80°C.

general nature of the relationship among substantivity, liquor ratio, and exhaustion percentage at equilibrium.<sup>10</sup> From Table I, it is obvious that the increase of  $K$  values is in the order of untreated < [Bmim]Br < [Emim]Br < [Bmim]Ac < [Emim]Ac. Consequently, it is concluded that the increase in improving dyeing rate and equilibrium exhaustion of wool under the same treatment condition is the order of [Bmim]Br < [Emim]Br < [Bmim]Ac < [Emim]Ac. The improved dyeing rate is mainly caused by the change of adsorption and diffusion mode of dye molecules. Before IL treatment, the surface hydrophobicity greatly hinders the adsorption of hydrophilic dye molecules; the intact and compact cuticle makes dye molecules diffuse into the fiber not in vertical diffusion but in the intercellular cement diffusion.<sup>29</sup> IL treatment makes wool cuticles eroded and even dissolved out, which is verified by SEM. After IL treatment, the surface hydrophilicity



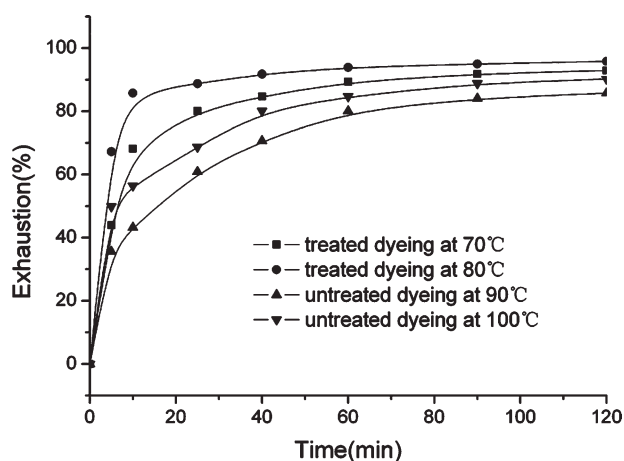
**Figure 4** Exhaustion versus time for dyeing of wool fibers with [Emim]Br dyeing at 80°C.



**Figure 5** Exhaustion versus time for dyeing of wool fibers with [Bmim]Ac dyeing at 80°C.

is increased greatly. Dye molecules could easily attach and vertically diffuse into the fiber. So the diffusion of dye molecules into the fiber is the combination of intercellular diffusion and vertical diffusion, which result in improving dyeing rate. The increased equilibrium exhaustion of IL-treated samples could be ascribed to the increase of dye site ( $-NH_2$  group) numbers and the amorphous regions. ILs disrupt the hydrogen bonds and disulphide linkages in the cuticle, then swell and even dissolve the cuticle out so that more dye sites are released<sup>28</sup> and the amorphous regions are enlarged.<sup>22,29</sup>

To further investigate the influence of treatment condition on IL-treated wool dyeing properties, [Bmim]Br-, [Emim]Br-, and [Bmim]Ac-treated wool dyeing uptake curves are shown in Figures 3–5, respectively, while Table I lists the results of  $t_{1/2}$ ,  $E$  at  $E_m$  and  $K$  obtained from Figures 3–5. From Figure 3 and Table I, it is found that with [Bmim]Br



**Figure 6** Low temperature dyeing of EmimAc-treated sample.

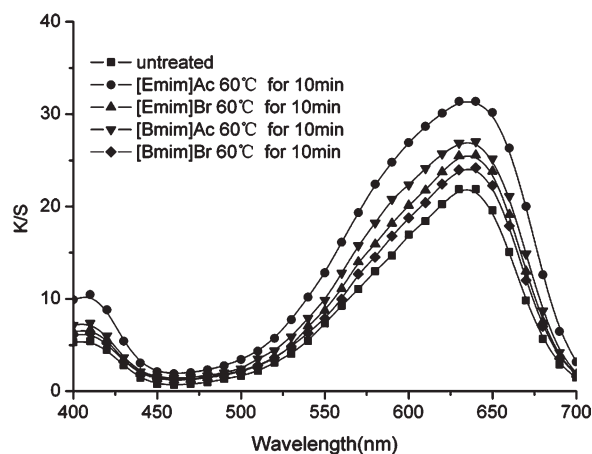


Figure 7 K/S values of dyed wool yarns.

treatment temperature increasing and time lengthening,  $E$  at  $E_m$  and  $K$  are slightly increasing in the order of  $60^\circ\text{C}$  for 10 min  $<$   $60^\circ\text{C}$  for 20 min  $<$   $80^\circ\text{C}$  for 10 min  $<$   $80^\circ\text{C}$  for 20 min. The same rule happens to [Emim]Br and [Bmim]Ac. It seems that treatment temperature plays more important role in improving the dyeability than treatment time. This is in good agreement with results obtained by Yuan et al.<sup>29</sup> Furthermore, Figure 3 reveals that five dyeing uptake curves are concentrated. Compared with Figure 3, Figures 4 and 5 show dyeing uptake curves are more scattered. In the case of [Emim]Ac, due to its better solubility, in violent conditions ( $60^\circ\text{C}$  for 20 min,  $80^\circ\text{C}$  for 10 min,  $80^\circ\text{C}$  for 20 min), wool yarns can be dissolved. Obviously, the anion category of IL plays a vital part in improving the dyeability of the wool fiber.

#### Low-temperature dyeing of wool after treatment

Recently, low-temperature dyeing has received increasing attentions due to its energy saving, and other advantages such as shrinkage prevention, comfortable wearability and bright shades.<sup>7</sup> The results of low temperature dyeing of the [Emim]Ac-treated sample are shown in Figure 6. It is evident that ini-

tial dyeing rate and equilibrium exhaustion of dyeing at  $70^\circ\text{C}$  and  $80^\circ\text{C}$  for treated samples are higher than that of conventional dyeing ( $90$ – $100^\circ\text{C}$ ) for the untreated sample. Modification of wool fiber surface by [Emim]Ac provides a valuable method for low-temperature dyeing at  $70^\circ\text{C}$ .

#### K/S and colorfastness

The dyeing property of the wool yarns was investigated in terms of the K/S curves. Generally, K/S is affected by the object nature, light, and dye concentration in the fiber. Herein, K/S is determined by dye concentration in the fiber because of equilibrium exhaustion. Figure 7 shows the increase of K/S at  $\lambda_{\text{max}}$  is in the order of untreated  $<$  [Bmim]Br  $<$  [Emim]Br  $<$  [Bmim]Ac  $<$  [Emim]Ac. It indicates that the acetate-based IL treated wool yarns give darker apparent shade depth than the bromo-based ILs treated samples. This result is in accordance with the results of dyeing exhaustion curves analysis and SEM.

The color fastnesses of all the wool yarns samples are listed in Table II. It can be concluded that the rubbing and washing fastness of wool yarns treated by [Bmim]Br, [Emim]Br, [Bmim]Ac are similar to the untreated wool yarns. However, wet color fastnesses of wool yarns treated by [Emim]Ac including rubbing and washing staining show a decrease of half grade. This is caused by the fact the wool fiber is too much eroded by [Emim]Ac [see Fig. 1(e)] and the fixed dye molecules are easily released from it when wetted.

#### CONCLUSIONS

This study reveals that ILs treatment can produce a remarkable modification of wool in the surface microstructure, thus significantly affect mechanical and dyeing properties. The results correspond to the SEM morphologies in which acetate-based ILs treated wool surface much more than bromo-based ILs. Comparable studies indicate that under the same treating condition (at  $60^\circ\text{C}$  for 10 min), wool

TABLE II  
Color Fastnesses of Dyed Wool Yarns

Sample	Abrasion fastness		Washing fastness					
	Dry	Wet	Color change	Staining cotton	Staining acetate fiber	Staining wool	Staining nylon	Staining polyester
Untreated	4	3–4	4	4–5	4	5	3–4	4–5
[Bmim]Br	4	3–4	4	4–5	4	5	3–4	4–5
[Emim]Br	4	3–4	4	4–5	4	5	3–4	4–5
[Bmim]Ac	4	3–4	4	4–5	4	5	3–4	4–5
[Emim]Ac	4	3	3–4	4	3–4	4–5	3	4

Note: Treatment condition of wool sample is at  $60^\circ\text{C}$  for 10 min.



samples treated with acetate-based ILS have higher initial dyeing rate, equilibrium exhaustion than that treated with bromo-based ILS, while the former owned less tensile strength than the latter. Temperature and time of treatment have more remarkable effect on mechanical and dyeing properties of wool treated by acetate-based ILS than that by bromo-based ILS. Due to [Emim]Ac-treated wool yarns having the best dyeing properties, the samples exhibit good low-temperature dyeing property. K/S and colorfastness investigations show that the wool yarns treated by the acetate-based ILS give darker apparent shades depth at the same dyeing conditions than that by the bromo-based ILS. The color fastnesses of wool samples treated by [Bmim]Br, [Emim]Br, and [Bmim]Ac have the same grades as the untreated sample except for a decrease of half grade in wet colorfastness of the wool sample by [Emim]Ac.

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