AUTEX 2022 Conference Proceedings 978-83-66741-75-1

DOI: 10.34658/9788366741751.126

HALOCHROMIC PROPERTIES OF A 5-AMINOIMIDAZOLE-4-CARBOXAMIDRAZONE AND ITS APPLICATION TO WOOL

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ABSTRACT

The application of stimuli-responsive molecules in textiles is an important field due to its potential in various areas of flexible sensing technology. In particular, pH plays an important role in nature, humans, and several processes. The pH of body fluids is one of the best indicators of disturbed health conditions. Thus, the development of textiles with halochromic properties has been increasingly attractive to display in real-time pH variations. Wool is one of the most important natural fibres because of its warmth and comfort. However, the dyeing process is costly and high energy-consuming. In this work, the halochromic properties under different buffers (acetate, phosphate, Britton-Robinson, artificial sweat, and artificial wound exudate) of a previously synthesized 5-aminoimidazole-4-carboxamidrazone were studied. Moreover, the first attempt to dye a wool knitted fabric with this molecule at a low temperature was performed. The developed material showed interesting halochromic properties (colourless in acidic pH and blue colour in the alkaline pH), even using artificial body fluids.

KEYWORDS

pH-responsive textiles, dyes, wool.

INTRODUCTION

Chromic molecules present a visual colour change when exposed to external stimuli and have received considerable attention for smart materials applications [1]. pH plays an important role in the human body, where several pH-dependent processes and reactions occur. Thus, controlling the pH of body fluids can be a suitable strategy to detect health problems (*e.g.* the measurement of the pH of sweat is useful to detect skin diseases, and the alkaline pH of wounds indicates infection and delayed healing).

Behind all the techniques developed for measuring the pH, the colour change remains one of the most cost-effective methods for real-time monitoring of the pH [2,3]. Thus, the development of new materials with halochromic properties has been increasingly attractive [4]. Amidrazones have been widely described due to their applications in many fields of chemistry, particularly in the synthesis of azo precursors [5,6]. These compounds are susceptible to oxidation and some of them have a very low oxidation potential [7].

Wool is one of the most popular natural fibres due to its natural properties such as warmth and comfort. Nevertheless, its dyeing process is costly and energy-consuming since it is usually performed at boiling or near-boiling temperature. Thus, the low-temperature dyeing of wool without agents is an urgent need [8].

In this work, the halochromic properties of a previously 5-aminoimidazole-4-carboxamidrazone synthesized by our research group were studied under different solutions from pH 3 to 12 using acetate, phosphate, Britton-Robinson, artificial sweat, and artificial wound exudate buffers. Then, the first attempt to dye wool with this amidrazone at a low temperature (40ºC) by exhaustion was performed. The solutions and the colour coordinates of the fabrics were measured by UV–vis spectrophotometry.

MATERIALS AND METHODS

1. Materials

Commercial wool jersey fabric with a weight per unit area of 160 $g \cdot m^{-2}$ was used in this work. First, the fabric was washed using a solution of 1.0 $g \cdot L^{-1}$ of a non-ionic detergent at 60 ºC for 60 minutes, rinsed with distilled water and dried. All reagents were purchased from Sigma-Aldrich without any purification.

2. Synthesis of the (*Z*)-5 amino-1-(4-methoxyphenyl)-*N*'-phenyl-1*H*-imidazole-4-carbohydrazonamide

The amidrazone was prepared according to a previous method developed by the research group with slight differences [9]. To a 25 mL flask containing 2.0 g of 5-amino-1-(4-methoxyphenyl)-1*H*-imidazole-4-carbimidoyl cyanide (8.3 mmol) and 10 µL of acetic acid in ethanol (8 mL) was added 1.25 mL of phenylhydrazine (12.5 mmol), under nitrogen atmosphere. The suspension was placed under magnetic stirring at a temperature of 8 °C for 17 hours. The compound was obtained in 94% yield (2.5 g; 7.8 mmol). The purity of this compound was proved by NMR (^1H) and elemental analysis. The NMR spectra was performed at room temperature on a Bruker Avance 3400 (^{1}H: 400 MHz). The data are reported by chemical shifts (ppm), multiplicity (s -singlet, brs - broad singlet d - doublet, t - triplet, dd - doublet of doublets or m - multiplet), the coupling constants (J) in hertz (Hz) and integration. Elemental analyses were performed on a LECO CHNS-932 instrument (University of Minho). ^{1}H RMN (400 MHz, DMSO-$d6$): δ 3.81 (s, 3H), 5.57 (brs, 2H), 5.77 (brs, 2H), 6.59 (t, J= 8.0 Hz, 1H), 6.84 (d, J= 7.9 Hz, 2H), 7.11 (t, J= 7.9 Hz, 4H), 7.31 (s, 1H), 7.44 (d, J= 8.7 Hz, 2H), 7.92 (s, 1H); Anal. calc. for $C_{17}H_{18}N_6O$: C, 63.34; H, 5.63; N, 26.07; found: C, 63.41; H, 5.62; N, 25.94.

3. Halochromic properties under different buffer solutions

UV-vis spectrophotometry (Shimadzu, UV-1800) was used to measure the absorbance spectra of the amidrazone under different buffer solutions with a standard quartz cuvette. The absorbance was measured in Britton-Robinson buffer (from pH 3 to 12), acetic acid-sodium acetate buffer (from pH 4 to 6), sodium phosphate buffer (from pH 6 to 8), artificial sweat (pH 4.3, 5.5, 8.0 and 6.5) and artificial wound exudate (pH 7.4). A starting solution of amidrazone (256 $mg.L^{-1}$) was prepared and diluted in 50% (v/v) with the corresponding buffer. A dilution only with water instead buffers was used as control.

4. Measurement of the colour of the wool samples

The colour strength of the wool samples was studied using a UV-2600, UV–vis spectrophotometer manufactured by SHIMADZU, using a D65 illuminant in the range from 400 to 800 nm. The colouring effects in CIE L* (lightness), a* (yellowness–blueness), and b* (redness–greenness) space were calculated using RGB values. The transmittance was measured (from 280 to 400 nm) and the Ultraviolet Protection Factor (UPF) was estimated according to the AATCC test method 183-2020.

RESULTS AND DISCUSSION

Wool knitted fabric was functionalized with (*Z*)-5-amino-1-(4-methoxyphenyl)-*N*'-phenyl-1*H*-imidazole-4-carbohydrazonamide previously synthesized by the research group [9]. This compound proved to be easily oxidized in contact with air and motivated the study of the colour under different buffer solutions (Britton-Robinson, acetate and phosphate). Moreover, artificial body fluids were also tested (artificial sweat and wound exudate). The UV-vis spectra of the solutions showed the emergence of a light pink colour under acidic conditions and a strong blue colour under neutral or slightly alkaline pH for Britton-Robinson and phosphate buffer (Figure 1-a). Only one exception was found using the artificial sweat at pH 7. In this case, a pink colour emerged, similarly to the acidic conditions, but more intense (Figure 1-a). The UV-vis spectra showed the appearance of an intense band around 595 nm with neutral or alkaline pH using the Britton-Robinson and phosphate buffer (Figures 1-b and c). Using the artificial sweat solutions from acidic to neutral pH, the band at 507 nm become more intense when the pH is increased. Under artificial sweat at pH 8 and artificial wound exudate, the band at 595 nm emerged again (Figure 1-d).

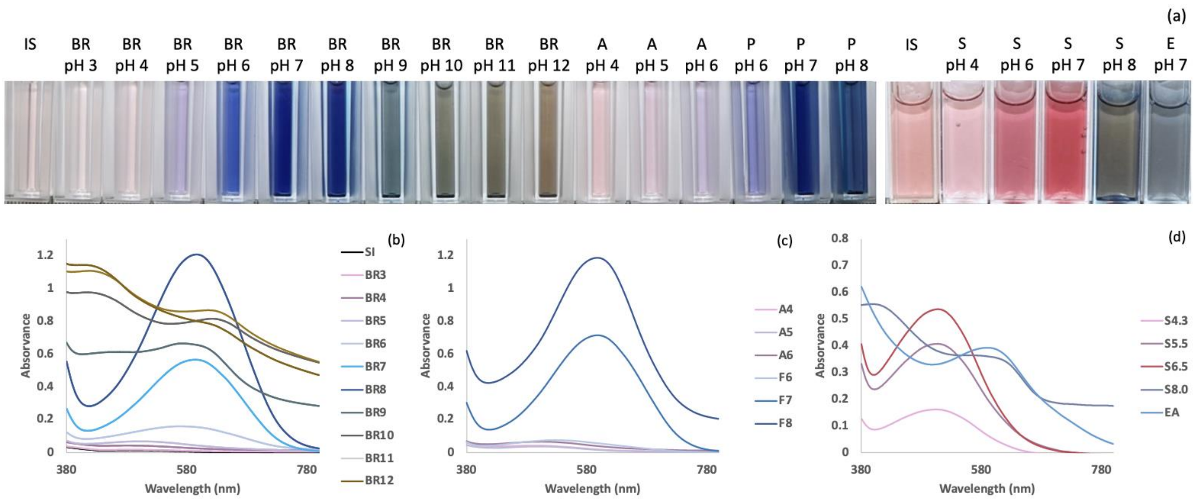

Figure 1. Colour changing of the amidrazone (*Z*)-5 amino-1-(4-methoxyphenyl)-*N*'-phenyl-1*H*-imidazole-4-carbohydrazonamide under the initial solution (IS) without buffers, Briton-Robinson buffer (BR), acetate buffer (A), phosphate buffer (P), artificial sweat (S) and artificial exudate (E) (a) and corresponding UV-vis spectra (b, c and d).

Then, the amidrazone was used to dye a wool knitted fabric with solutions obtained with Britton-Robinson buffers at pH 5 and 8 by exhaustion at 40ºC. The colour of the wool samples was assessed in the CIE L* (lightness), a* (redness-greenness), and b* (yellowness-blueness) space (Figures 2-a and b).

The colouration of the wool fabric changed from colourless, when acidic pH was used (Britton-Robinson buffer at pH 5 and the control initial solution (pH 3)), to blue when the alkaline buffer was used (Britton-Robinson buffer at pH 8) (Figure 2).

The UPF of the samples was calculated and compared with a control sample without amidrazone. The results showed that the functionalization increased the UPF from 15 (untreated wool) to 17-21 (wool dyed with amidrazone) (Figure 2-c). The best result was obtained in the sample prepared in alkaline conditions.

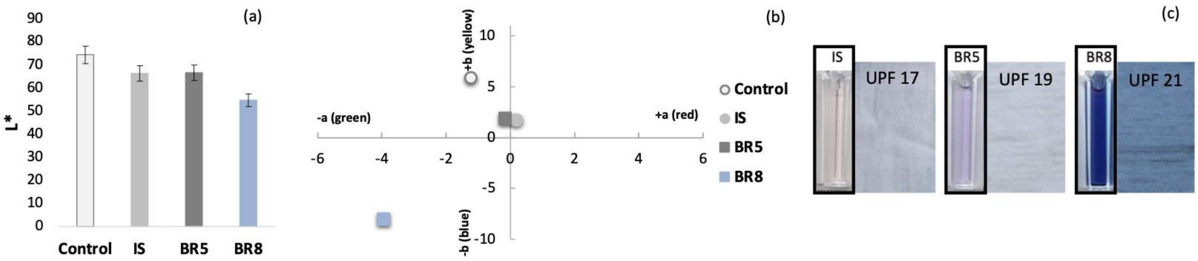

Figure 2. Colour coordinates of the wool samples (L* - lightness values, a* - yellowness-blueness and b* - redness-greenness) functionalized within amidrazone using the initial solution without buffers (IS) and using the Britton-Robinson buffers at pH 5 (BR5) and 8 (BR8).

CONCLUSION

The amidrazone (*Z*)-5-amino-1-(4-methoxyphenyl)-*N*'-phenyl-1*H*-imidazole-4-carbohydrazonamide was successfully applied on wool knitted fabric and showed interesting halochromic properties in acidic and alkaline conditions. Under acidic conditions the wool sample remained uncoloured and in alkaline conditions the colour changed to blue. In addition, the exhaustion process displayed good results at low temperature (40ºC). The functionalization also increased the UPF value of the wool from good to very good, according to AATCC 183-2020. This compound present high potential to be used as halochromic dyes for wool in functional textiles for sports, healthcare and sensors.

ACKNOWLEDGMENT

This work was funded by European Regional Development Fund through the Operational Competitiveness Program and the National Foundation for Science and Technology of Portugal (FCT) under the projects UID/CTM/00264/2021, UID/QUI/00686/2020, MEDCOR PTDC/CTM-TEX/1213/2020 and Ph.D. scholarship SFRH/BD/137668/2018.

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