



Halochromic properties of sulfonphthaleine dyes in a textile environment: The influence of substituents



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ABSTRACT

The application of pH-sensitive dye molecules onto textile materials is a promising method for the development of sensor materials. Ten commonly used pH-indicators, namely sulfonphthaleine dyes, are applied onto polyamide 6 using two distinct methods: conventional dyeing of fabrics and dye-doping of nanofibres. The influence of the substituents of each dye on their interaction with polyamide, as well as the difference between both application methods is investigated. For the conventionally dyed fabrics, halogen substituents are needed to result in a pH-sensitive fabric. This can be traced back to halogen bonding and is supported by theoretical simulations. Dye-doped nanofibrous non-wovens show significant dye leaching, which can be understood based on the very acidic electrospinning solution. The use of a complexing agent improves the leaching properties, especially for dyes containing four bromine substituents. These findings indicate the importance of halogen substituents on sulfonphthaleines for further research in the development of pH-sensitive sensors.

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1. Introduction

The colouring of textile materials is a widely applied and well-known process, wherein the focus is mainly on the development of dyes resulting in textile materials with constant colour [1,2]. Recently however, in the light of stimuli-responsive polymeric materials [3–7], an increasing interest is shown in the development of colour-changing materials such as pH-sensitive textiles [8–15]. These halochromic textiles can show an easily visible output signal in a non-destructive way. They also maintain all advantages of their parent materials: a textile sensor shows a high flexibility in contrast to conventional sensor systems. Furthermore, their applicability on large surfaces and the ability to give a local signal are great benefits

[16–30]. Possible applications include wound bandages and detection of acid vapours [13,31].

Herein, we focus on the application of sulfonphthaleine dyes on polyamide 6 (PA6). Sulfonphthaleine dyes form a relatively small dye class, but are widely used as acid–base indicators because they show a clear colour transition in function of pH. Therefore they find application in various other areas, such as detection of pesticides and CO₂, but also in biological and medical fields [32–51]. To utilise these dyes in textile sensors, a thorough understanding of their behaviour in aqueous solution is a prerequisite. Following our experience in studying a dye molecule in aqueous solution [14], a systematic study of ten commercially available sulfonphthaleine dyes was performed [15], wherein a clear influence of the substituents was found on the pH-sensitive behaviour (Fig. 1).

The colour changing mechanism of sulfonphthaleine dyes can be ascribed to a protonation/deprotonation reaction, as illustrated in Scheme 1. The dyes can exist in a neutral form (\mathbf{x}) in powder or in very acidic media. The most interesting molecular change (and thus colour change), however, is the deprotonation of a single anion (\mathbf{x}_a) to a resonance stabilised double anion (\mathbf{x}_b). The pK_a values given in

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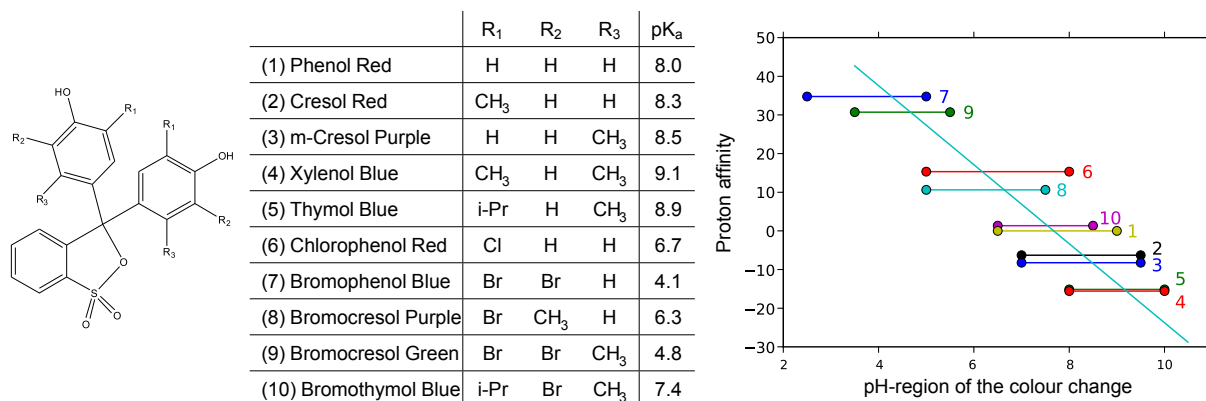
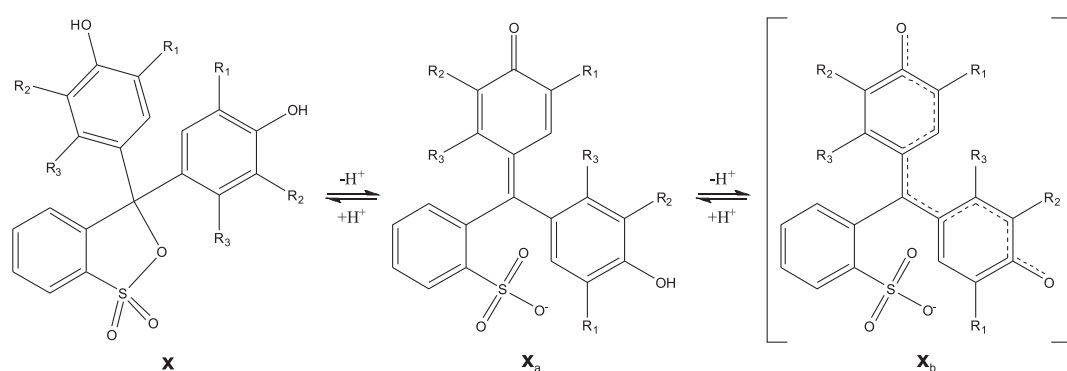


Fig. 1. Basic structure of sulfonphthaleine dyes and substituents of all studied molecules. The linear correlation between theoretical proton affinities and experimental pK_a's on the right hand side illustrates the large influence of substituents on the halochromic behaviour (adapted with permission from Ref. [15]).



Scheme 1. General colour changing mechanism for sulfonphthaleine dyes. While the neutral structure **x** is observed only in very acidic solutions or in powder, the relevant colour change originates from a deprotonation from the single anionic form **x_a** to a double anion **x_b**.

Fig. 1 are those of the deprotonation reaction from **x_a** to **x_b** and it can clearly be seen that the substituents have a large influence on the pH-region where this reaction happens. The molecular structure of these dyes is not only important for the observed colour transition, but also for the behaviour during the different dye application processes, as will be shown in this contribution.

Sulfonphthaleine dyes are applied onto PA6 in this work using two methods: conventional dyeing of fabrics and dye-doping of nanofibres. Nanofibres have a very small fibre diameter (and thus high specific surface area) [52], which results in very fast reaction times. This makes them very suitable as basis to develop halochromic sensors for wound healing and other optical applications [24,28,53–67]. Conventional fabrics have a slower reaction time because of their larger fibre diameter, but are ubiquitous, which is why they are also investigated here.

For the development of nanofibres, polyamide 6 and dye molecules are dissolved into a formic acid/acetic acid solution, which is then electrospun. During this very fast process (which occurs at room temperature), the solvent evaporates, forcing entrapment of the dye molecules in the fibres (see top of Fig. 2). Conventional dyeing of fabrics on the other hand is a diffusion process: during a relative long time (one hour) and at elevated temperature (100 °C) [68], the dye molecules are allowed to diffuse into the micro fibres from an aqueous solution at pH 5 (in the form of a fabric, see bottom of Fig. 2). Dye-fibre interactions are therefore the driving force for this dyeing process. The pH of both dyeing processes determines in which state the dye molecules will be (neutral, anion or dianion, see Scheme 1). This, combined with other differences such as fibre

diameter, will greatly influence the interactions between the dye and PA6. These will be analysed using UV/Vis spectroscopy and by performing dye leaching tests.

Further insight will be gained by applying molecular modelling, which is increasingly applied when studying dye molecules [69–71]. These simulations will provide insight on a molecular scale and help to understand the cause of a colour change [14,15]. The theoretical calculations in this work, which are all performed using Density Functional Theory (DFT), are utilised to gain a better understanding of the interaction of sulfonphthaleine dyes with the PA6 environment. This was previously successful to understand the experimentally observed pH-sensitive behaviour [28]. It has also been shown that M06-2X provides a good agreement with experiment when studying interactions, especially halogen bonding [72,73].

In a previous study, it was shown that the substituents of sulfonphthaleine dyes have a large influence on the pH-sensitive behaviour in aqueous solution [15]. The same ten molecules will now be applied onto PA6 to analyse the influence of these substituents on the interaction with PA6 and to study changes in pH-sensitive behaviour. Moreover, the dyeing will be performed in two different ways: conventional dyeing of fabrics (Section 4.1) and by dye-doping nanofibres (Section 4.2). The difference between these two methods is expected to have a large influence on the interaction, which is analysed by UV/Vis spectroscopy and dye leaching tests and will be further discussed in Section 4.3. As in our previous work, a combined experimental and theoretical approach is used to unravel the halochromic behaviour.

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