pH-sensitivity of azo dyes

Thierry De Meyer[1,2], Lien Van der Schueren[1], Karen Hemelsoet[2], Veronique Van Speybroeck[2], Karen De Clerck[1]
[1]Department of Textiles, Ghent University, Technologiepark 907, 9052 Zwijnaarde, Belgium
[2]Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium
Thierry.DeMeyer@UGent.be; Karen.DeClerck@UGent.be

OBJECTIVE

The purpose of the current paper is to study the influence of the environment (solution or textile matrix) onto the halochromic properties of azo dyes, using a combined experimental and theoretical approach.

INTRODUCTION

An increasing interest in colour changing textiles or so called chameleon textiles is recognized in the international literature since these textiles can be used as fast and simple sensor systems. Even though most attention has so far mainly been given to thermochromic and photochromic materials, halochromic textiles have potentials for many applications such as wound dressings and protective clothing.[1]

Recently, pH-indicators have been applied to textile materials, thus creating flexible sensors.[2-4] These textile sensors maintain all advantages of textile materials, meaning they are flexible, applicable on large surfaces and can give a local signal by local discolouration. This colour change is easy to perceive and can be used as a first warning signal. Besides textile materials, pH-indicators have been immobilized in several ways to create sensors for various applications.[5-7]

In this work, a combined experimental and theoretical approach will be used in order to gain a better understanding of the colour changing mechanism and the influence of the environment hereupon. The dye used in this work is ethyl orange (**EO**), which is a prototypical example of an azo dye (Figure 1). A starting point for this analysis is the dye in aqueous solution. The experimental work will mainly consist out of UV-VIS spectroscopy. Computational, static calculations will be used to analyse the colour changing mechanism and molecular dynamics simulations will be assessed to accurately reproduce the experimental spectra.

APPROACH

EO was supplied by Sigma-Aldrich and polyamide 6.6 (PA 6,6) by Concordia Textiles. Experimental UV-VIS spectra were measured by the spectrophotometer Lambda 900 from Perkin-Elmer. Transmission measurements in solution are recalculated to absorbance and reflection measurements on fabrics to Kubelka-Munk.

All *in vacuo* calculations in this research were carried out in Gaussian09,[8] using the B3LYP electronic structure

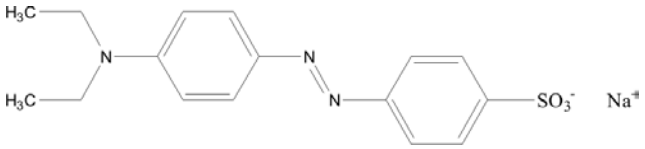

FIGURE 1: Lewis structure of ethyl orange (**EO**).

method with a 6-31+G(d,p) basis set. [9,10] Molecular Dynamics (MD) simulations were carried out in the CP2K software package, using the standard algorithms.[11] Ethyl orange (QM-level) is surrounded by a waterbox of 44.9 x 33.8 x 39.7 Å containing 1830 water molecules (MM-level). For the interaction between the QM and MM region, electrostatic embedding is used. Implicit solvation is modeled by using IEF-PCM and the SMD parameter set.[12] UV-VIS spectra were calculated with TD-DFT, using 30 excited states.

RESULTS AND DISCUSSION

Experimental spectra

Experimental UV-VIS spectra of **EO** as a function of pH were measured in aqueous solution and dyed onto PA 6,6,. In aqueous solution (Figure 2), the UV-VIS spectra clearly show a colour change: between pH 5 and 3 the colour of **EO** changes from orange to red (Figure 2).[5] In the visual area of the spectrum, Figure 2 shows a well-defined peak at 473 nm above pH 5. Below pH 5, the absorption peak shows a bathochromic shift to 508 nm. Here, the spectrum also shows a shoulder at 531 nm, which can point to two electronic structures. In the UV-area, the absorption peak shifts from 277 nm to 317 nm. These shifts clearly indicate a change in the electronic structure of the molecule which was confirmed by Raman spectroscopy.

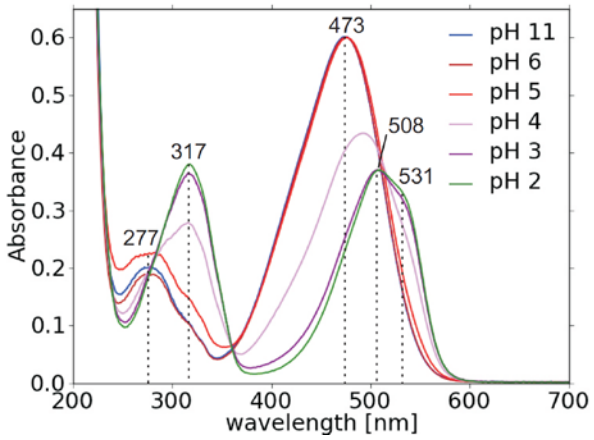

FIGURE 2: Experimental UV-VIS spectra of **EO** in aqueous solution at different pH values.

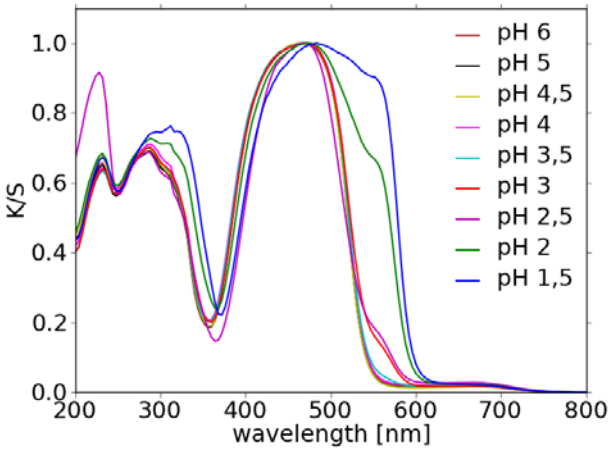

FIGURE 3: Experimental UV-VIS spectra of **EO** dyed onto PA 6,6 at different pH values.

Figure 3 shows that **EO** dyed onto PA 6,6 maintains a colour change, but at different pH values and between different colours. At this point, the exact nature of the involved species as well as the influence of the solvent or textile matrix are still unclear and therefore the parent **EO** compound, as well as possible singly and doubly protonated species will be examined in detail using DFT simulations.

Theoretical results

For details on the molecular simulations, the reader is referred to recently published work.[13] In this abstract, an overview of the main results will be given. Calculated wavelengths will be compared to experimental values to gain a better understanding in the molecular changes when changing the pH.

Based on the experimental results, a protonation on one (or two) of the nitrogen atoms of **EO** is a likely structural change. A first computational analysis can be made with static calculations in which only one geometry (lowest energy state) is considered. The optimized in vacuo structure (which is essentially considering the dye isolated in space) is depicted in Figure 4, as well as three possible protonation sites.

In vacuo energy calculations showed that protonation on site C (**EO**$_C$) is energetically most favourable. **EO**$_C$ will hence further on stand as model for the dye in acidic environment. In addition to the in vacuo calculations, an implicit solvent model can be used. In this model, a reaction field is placed around the molecule to mimic the electrostatic influence of the solvent. In both cases, the calculated maximum absorbance wavelengths are compared to the experimental values in Table I.

Because the results were still not satisfactory, a MD simulation was performed. MD simulations describe the time evolution of the geometry, taking the solvent into account explicitly. These simulations were performed for

FIGURE 4: Optimized in vacuo structure of EO with marked protonation sites

both **EO** and **EO**$_C$ and from each simulation, 100 snapshots were taken. For each snapshot, the UV-VIS spectrum was calculated using TD-DFT, of which the averages are given in Table I. The theoretical results almost coincide with the experimental values.[13]

TABLE I: Computed absorption maxima (in nm) of **EO** and **EO**$_C$ compared to experiment

Experimental values		Model compound	In vacuo	Implicit solvation	MD
pH > 5	473	**EO**	411	453	476
pH < 3	508	**EO**$_C$	497	470	508

Based on these promising results, further research will be carried out to better understand the effect of polyamide fibres on the halochromism of EO.

CONCLUSIONS

In this work, a combined experimental and theoretical approach was used to unravel the pH-sensitive behaviour of ethyl orange (**EO**). Based on experimental results, a theoretical method is proposed describing not only the neutral but also the protonated form of **EO.** This model thus accurately describes the halochromic behaviour of azo dyes and can be expanded to include the interaction with textile fibers in further research.

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