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UV/Visible spectroscopic studies of the effects of common salt and urea upon reactive dye solutions

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Abstract

The absorption spectra of two reactive dyes were studied by UV/Visible spectrophotometry in the presence of sodium chloride and urea at varying concentrations. Evidence has been produced to show that the effect of adding common salt to a dyebath at neutral pH is to produce increased aggregation of the dye species. In contrast, the addition of urea to a dye liquor results in reduced dye aggregation and the generation of increased amounts of the monomeric species. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The dyeing and finishing industry uses large quantities of salt in exhaust dyeing and urea in continuous dyeing and printing processes with anionic, water soluble reactive dyes. It is generally accepted that the addition of sodium chloride to a dyebath has the effect of increasing the degree of aggregation of the dye molecules via the common ion effect. This would have the effect of promoting the exhaustion of the dye onto the fibre, since suppression of the ionisation of the dye in solution effectively reduces the solubility imparted to it through its sulfonate groups. This reduction in solubility modifies the solution equilibrium in favour of the movement of dye aggregates from the solution to the fibre. In practice, the object is to use the optimum quantity of salt to produce the desired level of exhaustion: too little, and its effect will not be noticeable; too much and aggregate formation will be caused to such an extent that precipitation occurs. Alternatively if the aggregates become too large to diffuse within the fibre matrix, surface coloration only occurs [1]. Therefore it is currently thought that the 'salting on' effect is a result of interactions between the dye and electrolyte.

Iyer et al. have proposed that the dye adsorption increases as the disrupting effect of the electrolyte cations on water increases [2]. Studies by various researchers [3,4] have shown that the dye binding process within different dye–fibre systems is influenced by the structure of the water around the dye molecule and fibre surfaces.

One may visualise the role of the cation as perturbing the intermolecular hydrogen bonds between the water molecules. However the cations do not have the ability to perturb the water bound to the cellulose matrix since work performed by

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James and Frost [5] and Tait et al. [6] has indicated that the water–cellulose interactions are much stronger than the intermolecular water–water interactions.

Salt is regarded as fulfilling two main roles:

- To cause a shift in the equilibrium position of the dye and its aggregates in solution in favour of the fibre surface via the common ion effect.
- To compensate for the unfavourable effects of the repulsions caused by the interaction of the dye anions and the (slightly) negatively charged cellulose, i.e. 'masking' the surface potentials of the interacting species by cation binding.

In contrast, urea tends to be used as an additive in the continuous dyeing and printing of cellulose with anionic reactive dyes since good solubility is a pre-requisite for successful coloration. This can be achieved by the addition of a chemical that effectively increases the solubility of the dye thus leading to a more uniform dyeing and increased colour yield. Such hydrotropic agents act as an amphiphilic bridge between the solubilised dye and the aqueous media [7]. The efficacy of urea in increasing the bonded dye yield has been attributed to several factors:

- Swelling of the cellulose [8,9].
- Disaggregation of the dye, leading to increased solubility [8,9].
- Improved diffusion of the dye [8,9].
- Retarding the rate of water removal during drying [8,9].
- Acting as a solvent [8].

The results presented by Kissa [8] and the experimental data of others show that urea can increase the yield of the reaction between dye and cellulose only when the dye diffusion is limited by insufficient dye solubility. According to Fick's law, the diffusion rate ($\mathrm{d}s/\mathrm{d}t$) of the dye across the fibre surface area (A) is proportional to the dye concentration gradient ($\mathrm{d}c/\mathrm{d}x$) at the surface.

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -DA\cdot\frac{\mathrm{d}c}{\mathrm{d}x}.$$

The amount of dye diffusing into the fibre across area A during the entire dyeing process could be increased by:

1. increasing the diffusion coefficient (D) or the dye concentration gradient;
2. increasing the diffusion time (t).

Baumgarte concluded that the effect of urea on dye diffusion rates is only significant in special cases, the apparent diffusion coefficient being dependent upon dye concentration [10]. Thus an increase in urea concentration with the corresponding increase in dye solubility will cause an increase in the dye concentration. Urea, as a non-volatile solvent at ambient temperature, maintains swelling of the fibre, keeps the dye in solution and hence increases the diffusion time during which the dye is delivered to the interior of the fibre. Thus the effect of urea on dye diffusion cannot be separated from its solvent effects [8].

Hence, the use of salt in exhaust dyeing influences exhaustion by increasing the degree of aggregation. In contrast, the use of urea in pad applications increases the solubility of the dye by decreasing the degree of aggregation.

It is apparent from the above discussion and work performed by Guo et al. [11] that UV/visible spectroscopy can be used to ascertain the role of each of the additives. Where visible spectra show two adsorption maxima, *e.g.* red azo dyestuffs based on H-acid, these have been assigned according to previous literature references [12] [13]. The one at shorter wavelength has been assigned to soluble aggregated species [14–17] whilst that at longer wavelength to the monomeric species. It is the aim of this paper to utilise this technique to predict the effects of salt and urea on dyeing performance and to study how the effects change with increasing concentration of each of the two additives.

2. Experimental

Dyes: Remazol Red F-3B (C.I. Reactive Red 180) (Fig. 1(a)) was provided by DyStar and Procion Red MX-5B (C.I. Reactive Red 2) (Fig. 1(b)) was provided by BASF. The structures of both

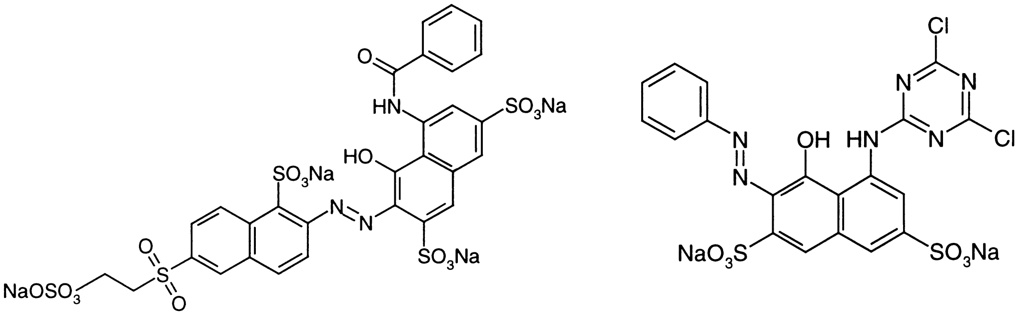

Fig. 1. (a) Remazol Red F-3B. (b) Procion Red MX-5B.

dyes are shown below in their azo tautomeric form. Although these commercial samples contain inorganic salts and organic formulating agents the dyes have been used without further purification.

Spectrophotometric studies: Spectra were recorded at room temperature on a Philips PU 8720 UV/VIS scanning spectrophotometer using a 5 mm glass cell in the 400–600 nm range. Beer's law experiments were performed using 2 ml of stock solution (6.5×10^{-4} M Procion Red MX-5B; 3.75×10^{-4} M Remazol Red F-3B), serially diluted with equal volumes of water. Experiments to study the effect of the additives were performed at a given dye concentration (6.5×10^{-4} M Procion Red MX-5B; 3.75×10^{-4} M Remazol Red F-3B) and varying either the salt or urea concentration in the range 20–120 g l^{-1}. To a 2 ml aliquot of an additive solution was added 2 ml of stock dye solution and the spectrum recorded.

3. Results and discussion

The linear nature of the plot of absorbance against dye concentration (Figs. 2 and 3) indicated that both dyes obeyed the 'Beer–Lambert' law

$$A = \varepsilon c l,$$

where A is the absorbance, c is the concentration mol^{-1}, l the pathlength in centimetres and the molar extinction coefficient.

The results of this UV/Visible spectroscopic study on the two dyes in the presence of salt and

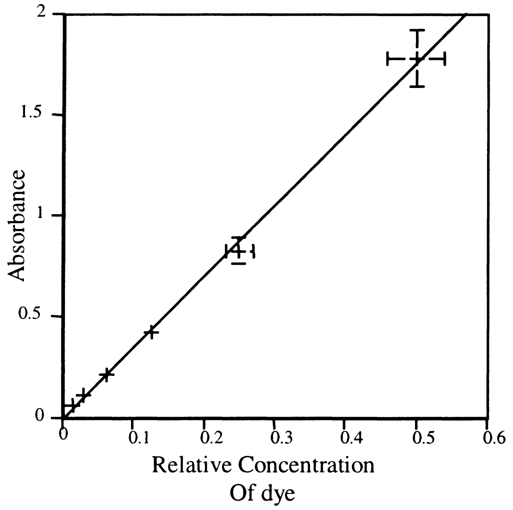

Fig. 2. Remazol Red F-3B.

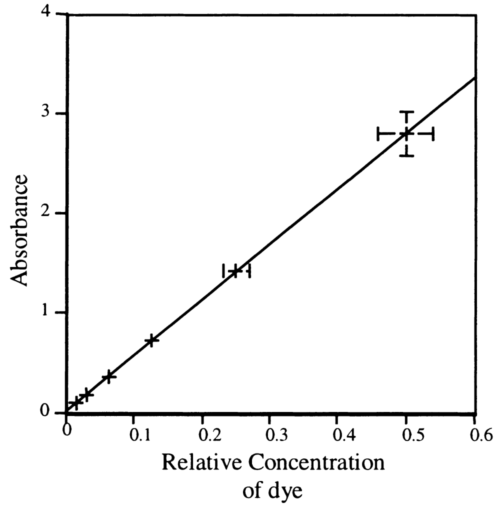

Fig. 3. Procion Red MX-5B.

urea were consistent with earlier literature results in showing that common salt exerted an aggregating effect upon the reactive dye species [13] and urea exerted a disaggregating effect [8,9,12,13,18].

Evidence of aggregation can be seen very clearly with both dyes in the presence of 60 g l^{-1} salt; the total absorbance decreases, implying that there are less absorbing species present in solution. In the presence of salt, the absorptions at 540 nm for Remazol Red F-3B and 539 nm for Procion Red MX-5B, corresponding to the monomer peaks, show a decrease in absorption (hypochromic shift). In addition, the soluble aggregate peak at 514 nm for Remazol Red F-3B and 513 nm for Procion Red MX-5B shows a corresponding increase in absorption (hyperchromic shift) relative to that of the monomer (Fig. 4). This suggests the generation of larger soluble aggregates on addition of salt to the original dyebath solution.

The literature states that one of the effects of urea is to increase the solubility of the dye by bringing about the disaggregation of the aggregated species present in solution at equilibrium [8,9].

This is particularly noticeable in the case of Procion Red MX-5B which displays a marked increase both in total absorbance and in the ratio of monomer to soluble aggregate concentration. The effect was much less marked in the case of Remazol Red F-3B, with only a small increase in the ratio of monomer to soluble aggregate species being observed on addition of 60 g l^{-1} urea.

Hence the addition 60 g l^{-1} urea to a dye liquor of Remazol Red F-3B (3.75×10^{-4} M, 0.31 g l^{-1}) will have little or no disaggregating effect. However the addition of 60 g l^{-1} urea to a dye liquor of Procion Red MX-5B (6.5×10^{-4} M, 0.37 g l^{-1}) will have a more significant effect.

The visible spectrum in the presence of urea also shows a slight bathochromic shift, compared with water alone, which may be attributed to a solvatochromic effect.

These conclusions relating to the effects of salt and urea on the two dyes can also be drawn from an examination of the relationship between the *change in molar extinction coefficient* (d) of both the soluble aggregate and monomeric species with different concentrations of additive.

(i) Influence of salt on molar extinction coefficient: If $_{aw}$ is molar extinction coefficient of the soluble aggregate in water, $_{as}$ molar extinction

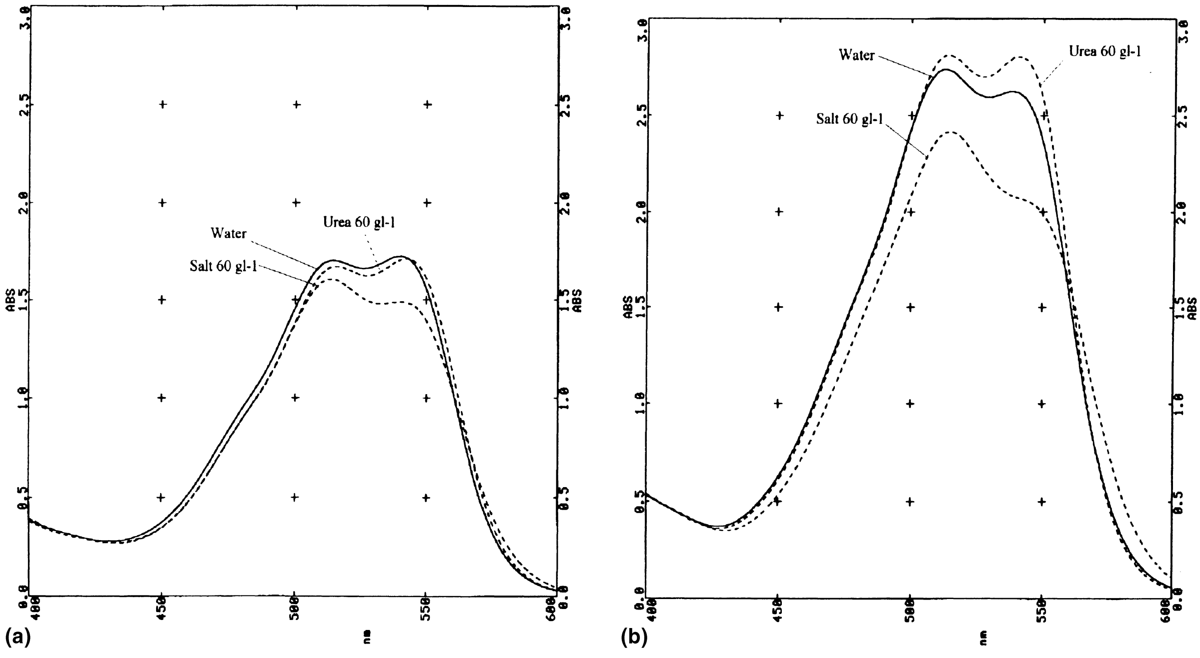

Fig. 4. (a) Remazol Red F-3B. (b) Procion Red MX-5B.

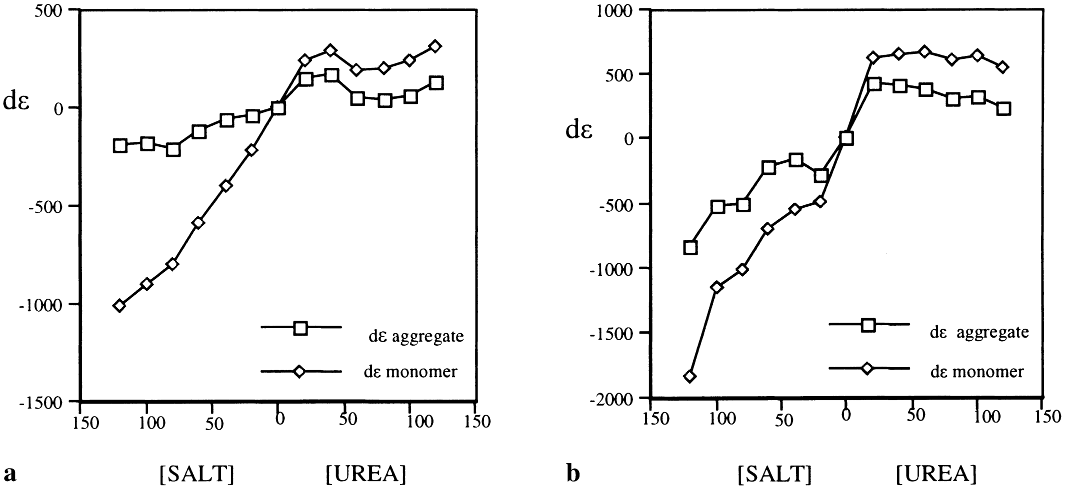

Fig. 5. (a) Remazol Red F-3B. (b) Procion Red MX-5B.

coefficient of the soluble aggregate in salt solution, then d_{as}, the *change* in the molar extinction coefficient of the soluble aggregate on addition of salt is given by

$$d\varepsilon_{\mathrm{as}} = \varepsilon_{\mathrm{as}} - \varepsilon_{\mathrm{aw}}.$$

Similarly, the change in molar extinction coefficient of the monomer on addition of salt, d_{ms}, is given by

$$d\varepsilon_{\mathrm{ms}} = \varepsilon_{\mathrm{ms}} - \varepsilon_{\mathrm{mw}}.$$

(ii) Influence of urea on molar extinction coefficient: If $_{\mathrm{au}}$ is molar extinction coefficient of the soluble aggregate in the presence of urea, $_{\mathrm{mu}}$ molar extinction coefficient of the monomer in the presence of urea, then d_{au}, the change in the molar extinction coefficient of the soluble aggregates in the presence of urea, is given by

$$d\varepsilon_{\mathrm{au}} = \varepsilon_{\mathrm{au}} - \varepsilon_{\mathrm{aw}}.$$

Similarly, the change in molar extinction coefficient of the monomeric species on addition of urea is given by

$$d\varepsilon_{\mathrm{mu}} = \varepsilon_{\mathrm{mu}} - \varepsilon_{\mathrm{mw}}.$$

Fig. 5(a), for Remazol Red F-3B, indicates a very modest decrease in molar extinction coefficient for the soluble aggregate species on addition of increasing concentrations of salt. However a much more marked decrease is observed for the monomeric species.

Fig. 5(b), indicates that Procion Red MX-5B is much more salt sensitive. The greater decrease in molar extinction coefficient suggests that monomeric species are being replaced by soluble aggregates as the concentration of salt increases.

In the case of Procion MX-5B, the addition of increasing concentrations of urea produces a more dramatic increase in concentration of both monomer and soluble aggregates than with Remazol Red F-3B. Both products at the concentration of dye used only need approximately 50 g l^{-1} of urea to optimise the amount of disaggregation.

The study suggests that Remazol Red F-3B is both less ‘salt sensitive’ and less responsive to urea than Procion MX-5B, technical features well known to batchwise and continuous dyers of cotton.

4. Conclusions

UV/Visible spectroscopy has been used as a method for determining the effects of salt and urea on two water soluble reactive red dyes in solution. Salt has the effect of increasing the degree of aggregation of the dye species present within the dyebath. This is shown by the decrease in the $_{\text{max}}$ of both the monomeric and, to a lesser extent, the soluble aggregate species of the dyes. Urea has the converse effect to salt, in that it increases the concentration of monomeric species in solution. This is evidenced by the increase in the $_{\text{max}}$ of the monomeric species relative to that of the soluble aggregate species. This technique may be used to assess the salt/urea sensitivity of reactive dyes and thereby help to define conditions for their efficient application to cellulose.

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