

## The Influence of NaCl Concentration on the Build-Up Properties and Aggregation of Reactive Dyes

Jantip Suesat

### ABSTRACT

This research investigated the influence of NaCl salt concentrations on the build-up properties of the selected warm- (Remazol Red RGB and Sumifix Supra Red 3BF) and hot- (Procion Red H-E3B and Drimarene Red X-6BN) dyeing reactive dyes on cotton. The results showed that an increment in the NaCl salt concentration in the dyebath influenced the visual color yields of the dyes on cotton. Too high a salt content led to a decline in the visual color yields. This may have been explained by the formation of larger dye aggregates, being enhanced by the higher salt content. Too large aggregates were considered to lead to a lower number of dyes diffusing into the fiber and so they would mostly remain on the fiber surface, thereby reducing the visual color yield. A significant reduction in visual color yield of the dyes on cotton occurred at 300 g/l salt. Among the dyes studied, Drimarene Red X-6BN was less affected by the salt concentration changes. From the study of the aggregation of the dye molecules in solution, it was found that increasing the salt concentrations enhanced the aggregation of the dye molecules. In the presence of salt, less dye in monomeric form existed in the solutions. When salt concentrations increased, the absorbance peaks responsible for the dye aggregates increased compared with those of the dyes in monomeric form. In addition, a bathochromic shift was also observed. With increasing salt concentrations, Drimarene Red X-6BN exhibited less reduction in the absorbance peak of the dye aggregates compared with the other dyes. This was in agreement with the build-up results. From this research, it showed that almost all recommended salt concentrations used in the reactive dyeing were not the optimum concentrations delivering the ultimate build-up of the dyes on cotton.

**Key words:** NaCl salt, reactive dyes, build-up, color yield, cotton

### INTRODUCTION

Reactive dye is the most important dye used for dyeing cellulosic fibers. With its outstanding wet-fastness properties, reactive dye holds the top market share for dyes in the textile-dyeing industry to date. In reactive dyeing, assisting agents are added into the dyebath in order to facilitate the dyeing process. Salt is added to the reactive dyebath to aid the exhaustion of the

dyes into the fiber. The commonly used salts are NaCl (common salt) and Na<sub>2</sub>SO<sub>4</sub> (Glauber's salt). In the dyebath solution, the dye molecules ionize into negatively charged molecules. The surface of the cellulosic fibers also ionizes in water into negative charges, restricting entry of the dye molecules due to the charge barrier. Thus, salt is added to the dyebath to neutralize the negative charges on the fiber surface so that the dyes can diffuse more easily into the fiber. Once the dye

molecules have been properly exhausted onto the fiber, alkali is added and the fixation of the dye molecules on the fiber takes place.

Reactive dye has a small molecular size compared with direct dye so therefore its substantivity is always lower. The dyes with lower substantivity show a preference to stay in the solution rather than entering the fiber. The more the dye stays in the dyebath solution, the more chance there is for the dye molecules to be hydrolyzed (Burkinshaw *et al.*, 2000). In order to gain adequate substantivity of reactive dyes toward cellulosic fibers, it is necessary to add an appropriate amount of salt into the dyebath (Bae *et al.*, 1997). Hamlin *et al.* (1999) investigated the influence of NaCl salt and urea on the characteristics of two reactive dye solutions: viz. Remazol Red F-3B and Procion Red MX-5B, using UV/Visible spectrophotometer. It was claimed that salt caused a decrease in the solubility of the dyes in solutions and the formation of dye aggregates whereas urea influenced the dye solutions in the opposite way. It was found that NaCl salt and urea exhibited more of an effect on the solution of Procion Red MX-5B than on Remazol Red F-3B.

Yeung and Shang (1999) studied the effect of metal ions on the hydrophobicity and aggregation of Procion Red MX-5B in silk dyeing. The study was conducted using  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . It was shown that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were able to induce more aggregation of the dye molecules than  $\text{Na}^+$  and affected the hydrophobicity of the dye in solution in a way that depended on the pH values. Metal ions exhibited a negative effect on the dyeing properties of Procion Red MX-5B on silk under acidic conditions whereas the opposite results were found when dyeing under alkaline conditions. However, too many metal ions used caused the precipitation of the dye molecules. The number of solubilizing groups on the dye molecules also influenced the dyeability of reactive dyes. Biolchi *et al.* (2006) reported that

increasing the number of sulfonate groups on the reactive dye molecules could lead to a reduction of dye exhaustion and fixation efficiency on the fiber. This was claimed to be caused by the increase in negative charges on the dye molecules. The greater the negative charges on the dye molecules, the greater the repulsion force between the dye molecules and the fiber. Nevertheless, the effect of the number of sulphonate groups on the dye fixation efficiency could be reduced by increasing the number of reactive groups on the dye molecules. Increasing the sulphonate groups whilst increasing the reactive groups on the dye molecules would have less effect on the dyeability of the reactive dyes. Apart from the solubilizing groups, the anionic groups in cellulose can also affect the adsorption of the reactive dye onto cellulose (Bae *et al.*, 1998). Anionic groups in cellulose will repulse the anionic solubilizing groups of reactive dye molecules thereby restricting the adsorption of the dyes onto the cellulose.

In the current study, the influence of NaCl salt concentrations on the build-up properties of reactive dyes on cotton was investigated. The reactive dyes selected for this study were warm-dyeing and hot-dyeing reactive red dyes. The optimum salt concentrations providing the highest color yields for each dye were determined. The effect of salt on aggregation of the dye was also investigated.

## MATERIALS AND METHODS

### Materials

The study used 40 Ne cotton knitted fabric. The warm-dyeing reactive dyes selected for this study were Remazol Red RGB and Sumifix Supra Red 3BF and the selected hot-dyeing reactive dyes used were Procion Red H-E3B and Drimarene Red X-6BN. The details of each dye used are shown in Table 1.

**Table 1** Warm-dyeing and hot-dyeing reactive dyes used.

Reactive dye type	Name of reactive dyes	C.I. Number	Manufacturer	Dyeing temperature (°C)
Warm-dyeing dyes	Ramazol Red RGB	N/A	Dystar	60
	Sumifix Supra Red 3BF	C.I. Reactive Red 195	Sumitomo	60
Hot-dyeing dyes	Procion Red H-E3B	C.I. Reactive Red 120	Dystar	80
	Drimarene Red X-6BN	N/A	Clariant	95

### Dyeing procedure

The 5 g pieces of cotton knitted fabric were dyed with selected reactive dyes to various depths of shade of 1, 2, 5, 7 and 9% based on the weight of fabric (% wof). At each depth of shade, the NaCl salt used was varied by 100, 150, 200 and 300 g/l, respectively. The dyeing was conducted using a UniDye Infra-red dyeing machine at a liquor ratio of 10:1. The dyeing was also performed using standard recommended salt concentrations (provided by the dye manufacturers) as a control. The alkali used for fixation was 15 g/l soda ash. Figure 1 illustrates the dyeing profile used in this study.

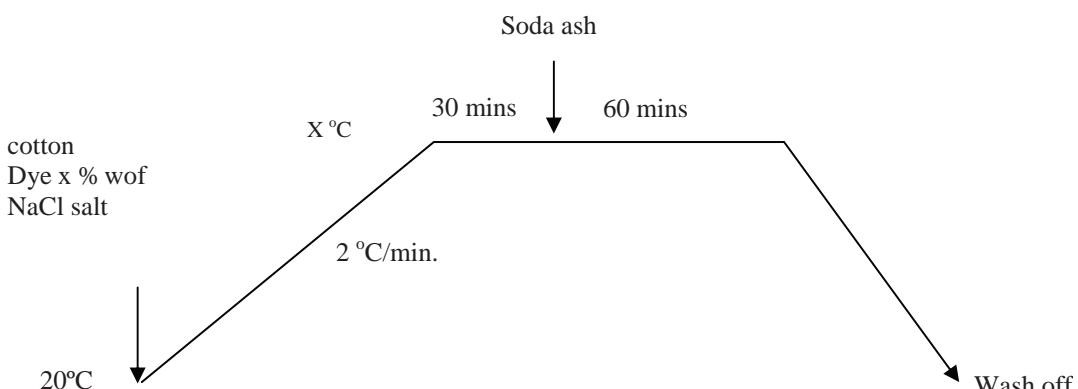
After dyeing, the fabrics were then rinsed in cold water for five minutes and boiled in a 1% soap solution for 15 minutes. The fabrics were, then rinsed in cold water until no color traces were observed in the rinsing water and then dried at room temperature.

### Measurement of visual color yield (K/S) on the dyed fabrics

The visual color yield of the dyed fabrics was measured and expressed as K/S values using a Macbeth ColorEye 7000 Spectrophotometer under illuminant D65 (Artificial daylight) at 10° standard observer. The mean comparisons of the K/S values at different salt concentrations were analyzed with one-way analysis of variance (ANOVA) using SPSS version 11.5 software. The mean differences were tested by LSD.

### Measurement of absorbance of dye solutions

Solutions of the four reactive dyes were prepared at a concentration of 0.02 g/l. Salt was added to achieve the solutions of each dye containing 50, 100 and 200 g/l salt. Dye solutions with no salt added were kept as a control. The absorbance curves of the dye solutions were determined using an UV/VIS spectrophotometer in the visible range (400-700 nm).

**Figure 1** Dyeing profile of reactive dyes on cotton.

## RESULTS AND DISCUSSION

### The influence of NaCl salt on the build-up properties of warm-dyeing dyes on cotton

At low percentage depth of shade, increasing the salt concentration caused an increase in the K/S values compared with the standard. When the dye applied increased to very high concentrations (7 and 9%), the color yields observed did not significantly increase from the standard and at the same time, there were adverse effect on color yields, especially at 200 and 300 g/l salt (Table 2). The decrease in the K/S values that occurred at high salt concentrations may have been due to a high degree of aggregation of the dye molecules in the dyebath. In the presence of salt, the dye molecules will tend to aggregate into a group and hold together (Johnson, 1989). At high level of percentage dye applied, the density of the dye molecules in the bath is high. This could reduce the amount of aggregation. The  $\text{Na}^+$  ions helped to reduce the repulsion between the negative charges of the dye molecules, so that they could get closer and become dye aggregates (Ingamells, 1993). Avery high salt concentration induces a greater aggregation of dye molecules, resulting in a larger size of dye aggregates which are unable to access the dye-fibers, causing a lower dye uptake on the fibers. These dyes will be left in the bath and lost as an effluent. Formation of too large dye aggregates leads to a precipitation of dyes

in the bath.

Dyeing with the standard salt concentrations (40-80 g/l) recommended by the dye manufacturer gave lower color yields of Remazol Red RGB on cotton fabrics compared with those dyed at 100, 150 and 200 g/l salt for 1-5% (wof) dye applied. At high percentage dye applied (7 and 9%), the recommended salt use was 100 g/l. Increasing the salt concentration had no positive effect on the color yields and at the same time caused an adverse effect when too much salt was added.

The build-up properties of Sumifix Supra Red 3BF were also investigated. Table 3 shows that the color yield of the fabric dyed using the recommended amount of salt was lower than that dyed using a salt concentration of up to 200 g/l. It indicated that the recommended salt concentrations for dyeing were not the optimum concentrations to achieve the highest color yield on cotton.

The increase in color yield with increasing salt content can be explained by an increase in dye exhaustion on the fiber as a result of salt. Salt assists the dyes to exhaust onto the fiber by reducing the negative charge repulsion between dye molecules and the fiber, thereby increasing the color yields (Ingamells, 1993). However, when the salt concentration was increased to 300 g/l, the color yield dropped significantly at all levels at depth of shade studied.

**Table 2** The visual color yields (K/S) of 1, 3, 5, 7 and 9% (wof) Remazol Red RGB dyed on cotton fabrics with 100, 150, 200 and 300 g/l salt in comparison with standard color yields.

Salt concentration (g/l)	K/S of the fabrics dyed at depth of shade (%)*				
	1	3	5	7	9
Standard	5.85 $\pm$ 0.21a	15.69 $\pm$ 0.40a	22.68 $\pm$ 0.18a	27.29 $\pm$ 0.16a	27.77 $\pm$ 0.23a
100	7.45 $\pm$ 0.64b	18.86 $\pm$ 0.21b	24.47 $\pm$ 0.85b	27.29 $\pm$ 0.16a	27.77 $\pm$ 0.23a
150	7.58 $\pm$ 0.25b	19.35 $\pm$ 0.64b	24.51 $\pm$ 0.28b	26.80 $\pm$ 0.29a	27.08 $\pm$ 0.17a
200	7.71 $\pm$ 0.21b	18.47 $\pm$ 0.14b	22.12 $\pm$ 0.25a	23.80 $\pm$ 0.28b	24.44 $\pm$ 0.63b
300	6.93 $\pm$ 0.10b	13.81 $\pm$ 0.71c	15.13 $\pm$ 0.53c	14.52 $\pm$ 0.73c	15.17 $\pm$ 0.38c

Means in the same column followed by different letter are significantly different ( $P \leq 0.05$ )

\*Means $\pm$  SD

It indicated that 300 g/l of salt was too high for this dyeing. When too much salt was present in the dyebath, the dye aggregates became larger. If the aggregates were too large, they were not able to diffuse into the fiber and instead were deposited on the fiber surface. These dye aggregates would dye only the fiber surface. If the dye aggregates were larger, their solubility in water was reduced and this resulted in the precipitation of the dyes. The dye uptake, thus, decrease. This was observed in the case of Remazol Red RGB.

### The influence of NaCl salt on the build-up properties of hot-dyeing dyes on cotton

A build-up study of selected hot-dyeing reactive dyes, Procion Red H-E3B and Drimarene Red X-6BN, was conducted on cotton fabrics. It was known that hot-dyeing reactive dyes are more

substantive to cotton than warm-dyeing reactive dyes. Therefore, they are expected to perform differently in the presence of NaCl salt. Procion Red H-E3B is dyed at 80°C whereas Drimarene Red X-6BN is dyed at an even higher temperature (95°C). From this difference in optimum dyeing temperatures, the differences in the substantivity and reactivity of these two dyes can be determined.

Table 4 shows the color yields of Procion Red H-E3B on cotton dyed at 1, 3, 5, 7 and 9% (wof) using 100, 150, 200 and 300 g/l salt changes in salt concentration affected the visual color yields of Procion Red H-E3B in a similar way as those seen with warm-dyeing dyes. However, the salt concentrations had less effect on the increment of color yield, especially at high levels of percentage dye applied (7 and 9%) compared with the warm-dyeing dyes. Moreover, with

**Table 3** The visual color yields (K/S) of 1, 3, 5, 7 and 9% (wof) Sumifix Supra Red 3BF dyed on cotton fabrics at 100, 150, 200 and 300 g/l salt in comparison with standard color yields.

Salt concentration (g/l)	K/S of the fabrics dyed at depth of shade (%)*				
	1	3	5	7	9
Standard	9.05±0.10a	21.75±0.25a	27.30±0.42a	28.59±0.11a	30.21±0.28a
100	11.31±0.45b	26.60±0.57b	33.13±0.21b	34.31±0.58b	35.19±0.41b
150	11.09±0.41b	28.14±0.47c	31.94±0.21c	32.55±0.14c	33.47±0.47c
200	11.17±0.19b	27.87±0.39bc	30.66±0.20d	32.58±0.21c	33.28±0.59c
300	7.86±0.20c	14.69±0.78d	15.05±0.38e	17.82±0.25d	18.44±0.47d

Means in the same column followed by different letter are significantly different ( $P \leq 0.05$ )

\*Means± SD

**Table 4** The visual color yields (K/S) of 1, 3, 5, 7 and 9% (wof) Procion Red H-E3B dyed on cotton fabrics at 100, 150, 200 and 300 g/l salt in comparison with standard color yields.

Salt concentration (g/l)	K/S of the fabrics dyed at depth of shade (%)*				
	1	3	5	7	9
Standard	8.16±0.13a	20.31±0.46a	28.47±0.04a	30.89±0.16a	32.65±0.08ab
100	9.80±0.71b	23.45±0.35b	29.79±0.71b	31.68±0.46a	33.19±0.14a
150	9.88±0.11b	24.49±0.28c	31.02±0.28c	31.47±0.64a	32.38±0.42b
200	9.84±0.57b	20.51±0.28a	22.28±0.11d	22.57±0.60b	22.64±0.35c
300	9.61±0.13b	11.74±0.14d	12.95±0.14e	12.87±0.49c	13.78±0.32d

Means in the same column followed by different letter are significantly different ( $P \leq 0.05$ )

\*Means± SD

increased salt content the color yield tended to decrease and this reduction of the color yield occurred at lower salt concentrations than those observed for warm-dyeing dyes. This suggested that the dye molecules seemed to aggregate more easily, so less salt was needed for the aggregate formation of Procion Red H-E3B dye molecules. Larger aggregates which were less capable of diffusing into the fiber were also expected to be formed in the presence of a lower amount of salt as compared with warm-dyeing dyes, leading to the decrease in color yield. Dyeing of Procion Red H-E3B using 300 g/l salt brought about a considerable decrease in color yield at all depths of shade. This may have been caused by the larger dye aggregate formation which was less capable of diffusing into the fiber and thus more dye was left in the bath.

Dyeing of Procion Red H-E3B using the standard salt concentrations (40-80 g/l) recommended by the dye manufacturer did not provide maximum color yields on cotton fabrics compared with those dyed at the various salt concentrations in this study. Unlike in the case of the warm-dyeing dyes, for the salt concentrations used in this study, increasing the salt concentration had a more negative effect on the color yield of the dyes on cotton. This may be explained by the fact that less salt was needed for dyeing Procion H-E3B, therefore, at the same level of salt, Procion Red H-E3B seemed to form larger aggregates than the

warm-dyeing dyes, leading to a salting-out effect.

Drimarene Red X-6BN is a hot-dyeing reactive dye with a dyeing temperature of 95°C (15°C higher than that of Procion Red H-E3B). The color yields of cotton fabrics dyed with Drimarene Red X-6BN are depicted in Table 5. The trends in the results are quite similar to those of the previous three dyes. The salt concentration of 300 g/l was too high for the successful dyeing of Drimarene Red X-6BN on cotton as seen in the reduced K/S values. The larger dye aggregates that formed are explained for the same reasons discussed earlier. In comparison with the other three dyes, Drimarene Red X-6BN seemed to be less affected by the salt concentrations, as there was less change in color yields. Drimarene Red X-6BN was less sensitive to salt concentrations than Procion Red H-E3B (the hot-dyeing dye with a lower dyeing temperature) and the two warm-dyeing dyes. This result corresponded to the work reported by Hamlin *et al.* (1999) which claimed that Remazol Red F-3 (warm-dyeing dye) was less sensitive to salt than the Procion Red MX-5B cold-dyeing dye. It indicated that dyes with a different degree of substantivity responded to NaCl concentrations differently. As with the other dyes, the standard recommended salt concentrations were not the optimum concentrations used to achieve maximum color yield of Drimarene Red X-6BN on cotton.

**Table 5** The visual color yields (K/S) of 1, 3, 5, 7 and 9% (wof) Drimarene Red X-6BN dyed on cotton fabrics at 100, 150, 200 and 300 g/l salt in comparison with standard color yields.

Salt concentration (g/l)	K/S of the fabrics dyed at depth of shade (%) <sup>*</sup>				
	1	3	5	7	9
Standard	6.73±0.11a	18.85±0.21a	25.75±0.08a	30.38±0.25a	32.80±0.14ab
100	7.28±0.01b	20.58±0.30b	28.27±0.33b	31.25±0.35b	32.82±0.14ab
150	8.36±0.11c	20.62±0.01b	28.76±0.08c	32.06±0.06c	33.31±0.35a
200	8.7±0.08d	22.33±0.03c	29.94±0.20d	31.56±0.08bc	32.53±0.14b
300	8.87±0.05e	21.55±0.21d	25.02±0.05e	27.04±0.07d	27.48±0.35c

Means in the same column followed by different letter are significantly different (P≤0.05)

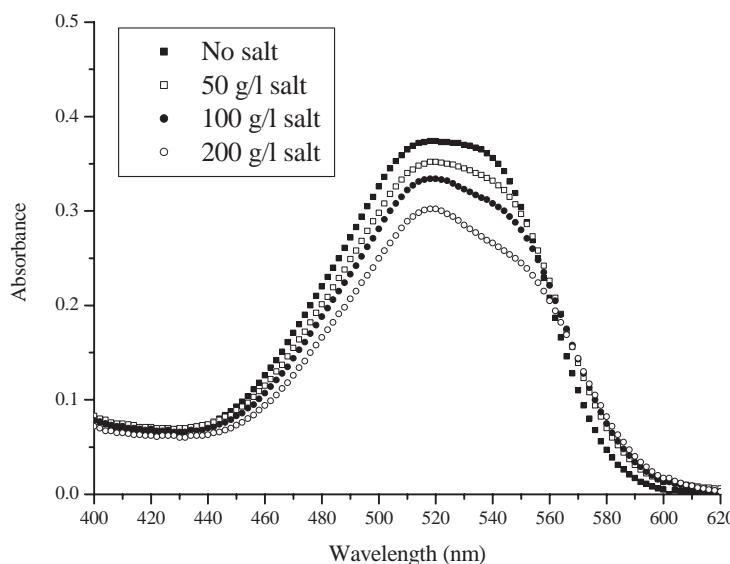
\*Means± SD

### Study of aggregation of dye molecules in the dye solutions.

From the previous study, the influence of salt concentrations on the build-up properties of the selected warm- and hot-dyeing reactive dyes was determined. The dyes responded to the change of salt concentration in a fairly similar manner. Further study was conducted on the effect of salt on the aggregation of each dye in solution. The experiment was carried out using 0.02 g/l dye solutions containing 0, 50, 100 and 200 g/l salt respectively and the absorbance of the solutions was then measured. Figures 2-5 show the change in the absorbance curves of the dye solutions as the salt concentration was increased, confirming that salt did affect the properties of the solutions of these reactive dyes.

The absorbance curve of the Remazol Red RGB solution in the presence of various salt concentrations is shown in Figure 2. It shows that increasing salt concentrations brought about a reduction in the total absorbance of the dye solution. This implied a lower number of absorbing dye species present in the solution when the salt content increased. It was considered to be due to the influence of salt on the solubility of the dye

molecules in the solution. These results were consistent with the works of Hamlin *et al.* (1999) which explained that salt had an effect on the aggregate formation of dye molecules which in turn, reduced the solubility of the dye in water. Furthermore, the absorbance curves exhibited a slight bathochromic shift when the concentrations of salt were increased. Remazol Red RGB exhibited two absorbance peaks. The absorption peak at 540 nm was expected to be the peak of dye molecules in monomeric form and the peak at 520 nm was the soluble dye aggregate peak (Hamlin *et al.*, 1999). When the concentrations of salt increased, the absorption peak of the monomeric dye species decreased (hypochromic shift) relative to that of the aggregate. The absorption peak of the soluble dye aggregates became dominant. This suggested that in the presence of higher salt concentrations, there was less dye in monomeric form in the dye solution. The dye molecules tended to stay in the form of aggregates. This was in agreement with the work done by Hihara *et al.* (2000) that showed increasing the NaCl concentrations promoted the aggregation of dyes.



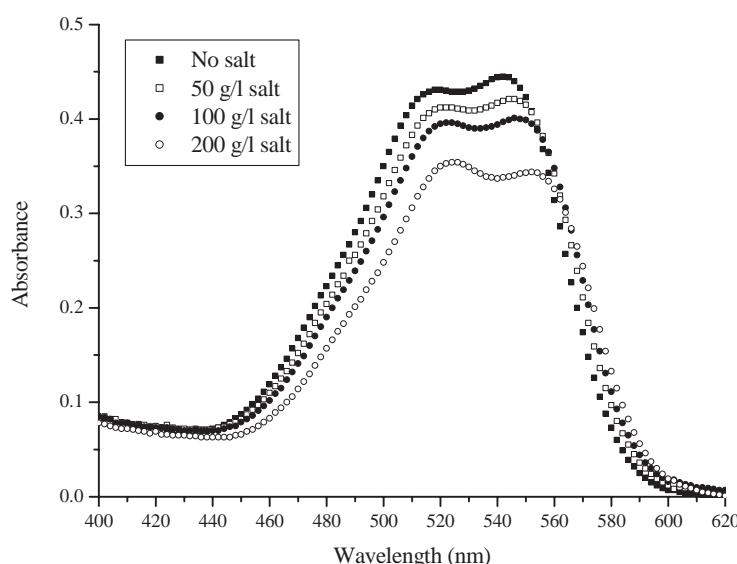
**Figure 2** Absorbance curves of 0.02 g/l Remazol Red RGB containing 0, 50, 100 and 200 g/l salt.

The aggregation study of Sumifix Supra Red 3BF in the presence of salt is illustrated by the change in absorbance curves as seen in Figure 3. From the information provided from the manufacturer, Sumifix Supra Red 3BF is known as a hetero-bifunctional dye which possesses vinylsulphone and monochlorotriazine reactive groups in the molecules.

The absorbance curves of Sumifix Supra Red 3BF shown in Figure 3. exhibited a reduction in total absorption intensity as the salt concentrations increased. The same reasons used in the case of Remazol Red RGB can be applied to this result, that salt induces the aggregation of the dye molecules and lowers their solubility, thereby causing a reduction of absorbing species. Thus, the absorbance of the dye solution reduced with the salt concentrations present in the solutions. Also, the curves show a slight bathochromic shift, similar to those of Remazol Red RGB. Sumifix Supra Red 3BF exhibited two absorption peaks at 520 and 544 nm. The absorption at 520 nm was the peak of the soluble dye aggregates and the peak at 544 nm was the monomeric dye species peak. In the absence of salt, the peak of the dye in monomeric form was

more dominant, indicating that with no salt present in the solution, dye molecules preferred to stay in monomeric form. With increasing salt concentrations, the peak of the monomeric dye species was gradually decreased (hypochromic shift) relative to the increase (hyperchromic shift) of the soluble aggregate peak. When the salt concentration added was 200 g/l, the absorption of the monomeric species was lower than that of the soluble aggregates. These results implied that the dye molecules tended to aggregate at higher salt concentrations.

The aggregation of dye molecules was also investigated for the two hot-dyeing dyes: Procion Red H-E3 and Drimarene Red X-6BN. The influence of salt concentrations on the absorbance of Procion Red H-E3B dye solutions is depicted in Figure 4. From the information provided, Procion Red H-E3B is a reactive dye containing bis-monochlorotriazine (bis-MCT) reactive groups. The absorbance curves of Procion Red H-E3B solution showed the same tendency observed in the two warm-dyeing dyes. The total absorbance decreased with increasing salt concentrations. The absorbance curves exhibited two peaks at 512 and 534 nm which were the peaks

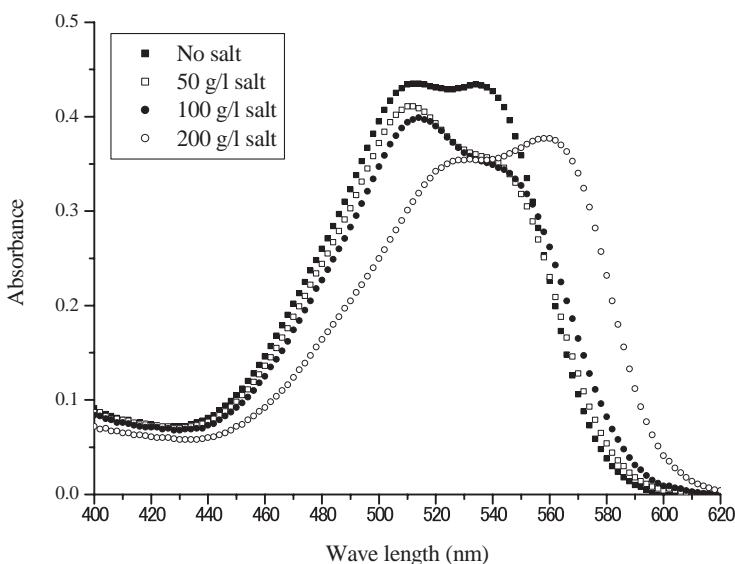


**Figure 3** Absorbance curves of 0.02 g/l Sumifix Supra Red 3BF containing 0, 50, 100 and 200 g/l salt.

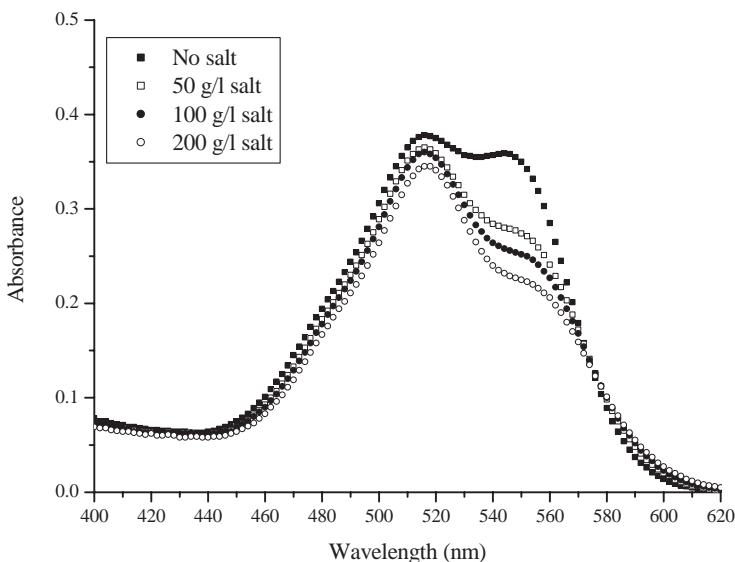
of the soluble aggregates and the monomeric dye species, respectively. A reduction in the absorbance of the monomeric dye species peak was observed relative to the soluble aggregate peak as the effect of salt. A drastic change in the absorbance curve of Procion Red H-E3B was obtained when 200 g/l salt was added to the solutions. The absorbance curves were shifted considerably to a longer wavelength. The absorbance peaks were shown

at 526 and 560 nm. This might have been due to the formation of larger dye aggregates, which caused the dye solutions to respond differently to the visible light. The obvious change in the absorbance curve of Procion Red H-E3B in the presence of 200 g/l salt could be observed visually from the change in the color of the solutions from bright red to ruby.

The results of Drimarene Red X-6BN are



**Figure 4** Absorbance curves of 0.02 g/l Procion Red H-E3B containing 0, 50, 100 and 200 g/l salt.



**Figure 5** Absorbance curves of 0.02 g/l Drimarene Red X-6BN containing 0, 50, 100 and 200 g/l salt.

illustrated in Figure 5. Drimarene Red X-6BN is known as a bis-MCT reactive dye (Phillips, 1998), and is sold as a dye mixture. The effect of salt concentrations on the absorption of the dye solutions was similar to that of the dyes studied previously. Drimarene Red X-6BN also exhibited two absorbance peaks. The first peak occurred at 516 nm which was responsible for the soluble aggregates and the peak at 544 nm belonged to the monomeric species. With no salt added, the absorbance peak of the soluble aggregates was higher than that of the monomeric dye species. This might have indicated that the dye molecules of Drimarene Red X-6BN preferred to stay in the aggregate form even in the absence of salt. Predictably, once the salt was added, a considerable decrease in the intensity of the monomer peak was noticed. This was caused by the aggregation of the dye molecules in the presence of salt. However, when the salt concentrations were increased further, there was only a subtle change in the absorption. It may be said that Drimarene Red X-6BN is less sensitive to the change in salt concentrations compared with the other reactive dyes used in this study.

From this study, it can be seen that NaCl salt has a significant effect on reactive dyeing. The salt caused aggregation of the dye molecules which affected the dyeability of the dyes on the targeting fibers in a way that enhanced the exhaustion of the dye into the substrates. The dye aggregates were less soluble than the dye molecules in monomeric form, thereby tending to absorb into the fibers rather than staying in the solutions. With a very high salt content present in the dye solutions, larger dye aggregates were formed. Too large aggregates were not be able to diffuse into the fiber, instead, they remained only on the fiber surface. The dyeing efficiency, as a result, was impaired. If the further addition of salt continued, large dye aggregates lost their solubility in water and then precipitated.

The different chemical nature of these

reactive dyes seemed to relate to their salt sensitivity. The dyes with different degree of substantivity and reactivity towards cotton fibers would respond to a change of salt concentrations to a differing extent. The hot-dyeing reactive dyes, which were more substantive to cotton fiber than the warm-dyeing reactive dyes tended to be less sensitive to the change of salt concentrations, confirmed by the results with Drimarene Red – X6BN. Furthermore recommended salt concentrations were not the optimum concentrations used to achieve maximum color yield of all the dyes at almost all depths of shade studied. However, using large amount of salt to obtain a slightly higher color yield on the fabrics may not be cost effective. The high salt content in an effluent drained from the dyeing process had an effect on the environment. On the other hand, if too low a salt content is employed, the amount of dye exhausted onto the cotton fiber would not be as required. The percentage dye fixation and percentage dye loss would have to be taken into account. This would lead to more dye being drained with the wastewater after dyeing. Although the amount of salt used is small, more dye left in the bath after dyeing can also cause environmental pollution. Therefore, the appropriate amount of salt used for the dyeing would have to be the one that renders both a satisfactory degree of color yield and cost effectiveness to the whole dyeing process.

## CONCLUSIONS

The study investigated the influence of salt concentrations on the build-up properties of the selected warm- and hot-dyeing reactive dyes on cotton. The results showed that the salt concentrations had an effect on the visual color yields of the reactive dyes obtained on cotton. The build-up properties of the warm-dyeing reactive dyes, Remazol Red RGB and Sumifix Supra Red 3BF and the hot-dyeing reactive dyes, Procion Red H-E3B and Drimarene Red X-6BN, were affected

by the salt concentrations in a similar manner. Drimarene Red X-6BN exhibited a lower sensitivity to the change in salt concentrations compared with the other three dyes. It might be said that Drimarene Red X-6BN was a less salt concentration-sensitive dye. However, too high a salt concentration led to an adverse effect on the build-up properties of the dyes, especially 300 g/l salt at which a drastic loss of dye-aggregate solubility took place and some dyes precipitated. As a result, the visual color yields obtained were impaired. The results indicated that almost all the recommended salt concentrations were not at the optimum concentrations to provide a maximum build-up of the reactive dyes on cotton. The optimum salt concentrations offering the highest visual color yields on cotton were often higher than those being recommended.

The influence of salt concentration on the aggregation of dye molecules supported the build-up results that increased of salt concentrations enhanced a greater aggregation of the dye molecules. With increasing salt concentrations, more dye aggregates were formed and less monomeric dye species was present in the solutions. This was observed by the change in the absorption peaks of the monomeric dye species and the soluble dye aggregates. The change in salt concentrations had less effect on the absorbance of Drimarene Red X-6BN solutions compared with the other dyes. This result was consistent with the build-up study. This confirmed that Drimarene Red X-6BN was less sensitive to salt concentrations.

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