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**Article:**

Burkinshaw, SM and Salihu, G (2019) The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres. Dyes and Pigments, 161. pp. 605-613. ISSN: 0143-7208

https://doi.org/10.1016/j.dyepig.2017.09.024

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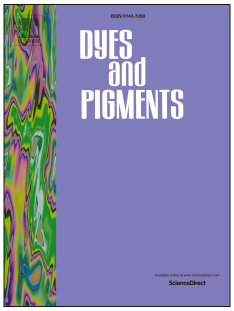

# The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres

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PII: S0143-7208(17)31777-1

DOI: 10.1016/j.dyepig.2017.09.024

Reference: DYPI 6249

To appear in: *Dyes and Pigments*

Received Date: 18 August 2017

Revised Date: 11 September 2017

Accepted Date: 11 September 2017

Please cite this article as: Burkinshaw SM, Salihu G, The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.09.024.

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# The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres

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## Abstract

A model is proposed to explain the manner by which the uptake of reactive dyes on cellulosic fibres is promoted by the addition of NaCl or $Na_2SO_4$ to the dyebath. The theoretical model invokes the concept of interstitial water in dyeing and suggest that increased dye uptake occurs because the added inorganic electrolyte promotes dye aggregation which reduces the solubility of the dye in the dyebath, so that the inherent preference of the highly soluble dye to favour the aqueous phase shifts towards the fibre phase. It is proposed that the same model can account for the promotion of direct dye uptake imparted by the reduction in the liquor ratio utilised for dyeing. As such, added inorganic electrolyte and reduced liquor ratio are considered to exert a combinatorial promotional effect on reactive dye uptake.

## Highlights

- the role of liquor ratio in reactive dye application is modelled
- interstitial water is used to show that low liquor ratio reduces dye solubility
- reducing liquor ratio promotes dye aggregation

## keyword

keywords: dyeing cotton; dyeing auxiliaries; electrolyte; reactive dyes; salt-free dyeing

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## 1 Introduction

Although several types of dyeing auxiliary are available that offer different kinds of assistance to immersion dyeing processes, the manner by which many auxiliaries function is unclear (1). An analysis (2) of published work relating to the role of the most important auxiliary utilised in the exhaust dyeing of cellulosic fibres with direct dyes, namely inorganic electrolyte (NaCl or $Na_2SO_4$), enabled a theoretical model to be devised (3), which invoked the concept of interstitial water, to explain the role of added NaCl or $Na_2SO_4$ in the application of direct dyes. The promotional effect of added inorganic electrolyte on direct dye uptake was considered to arise because of the combined effects of induced dye aggregation and consequent reduced dye solubility on the effective dye concentration gradient that exists between the amount of dye in the dyebath and the amount of dye in the fibre; two equations were derived to interpret this theoretical model of direct dye adsorption (3). The same theoretical model was also able to explain the promotional effect which reducing the liquor ratio used for dyeing has upon the uptake of direct dyes on cellulosic fibres and two equations were devised (4). The model was then employed to interpret the results obtained for a series of dyeings on cotton which had been carried out using commercial grade direct dyes, employing different liquor ratios in both the absence and presence of added NaCl (5). It was shown (5) that because adding inorganic electrolyte to a direct dye dyebath and reducing the liquor ratio used for dyeing achieve the same outcome, namely promotion of direct dye uptake, it is possible to dye cotton to realistic depths of shade using direct dyes in the absence of added inorganic electrolyte through the use of very low liquor ratios. In an attempt to clarify the manner by which added NaCl or $Na_2SO_4$ influences reactive dye uptake on cellulosic substrates, the previous part of the paper (6) presented an analysis of published research findings relating to the promotional impact of added inorganic electrolyte on reactive dye uptake.

In this part of the paper, the findings from this analysis (6) are used to develop a theoretical model which explains the promotional effect imparted by added inorganic electrolyte on reactive dye

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uptake; it will be shown that the same model can also explain the promotional impact of reduced liquor ratio on reactive dye uptake.

In the next part of the paper, experimental results obtained by applying commercial grade reactive dyes to cotton will be interpreted using the theoretical model so as to explain why it is possible to dye cotton (and other cellulosic fibres) using reactive dyes in the complete absence of added electrolyte at low liquor ratio.

## 2 reactive dyes and the use of added inorganic electrolyte

The essential features of reactive dyes, from the viewpoints of their structure and application, were discussed in the preceding part of the paper (6). Since their commercial introduction over 60 years ago, global consumption of this dye class on cotton and other cellulosic fibres has enjoyed steady growth with the result that reactive dyes nowadays account for ~ 55-60% of global dye consumption for cellulosic fibres (2).

Essentially, reactive dyes bear a close structural resemblance to direct dyes in that both types of dye are essentially long, planar, anionic molecules solubilised by one or more ionised sulfonate groups. However, in the case of reactive dyes, attached to the constituent chromogen (eg azo, AQ, etc.) is a reactive system that contains one or more electrophilic groups which enable the dyes to form a covalent bond with nucleophilic hydroxyl groups in the cellulosic substrate. Because the reactive dye is covalently attached to the cellulosic substrate, ensuing dyeings display characteristically very high levels of fastness to wet treatments, such as domestic washing, this being in sharp contrast to their direct dye counterparts, which characteristically exhibit only low to moderate wet fastness properties on cellulosic fibres.

To expedite dye-fibre reaction, reactive dyes are applied to cotton and other types of cellulosic fibre under aqueous alkaline (eg NaOH, $Na_2CO_3$) conditions so that the cellulosic hydroxyl groups (ie Cell-OH) are deprotonated, forming the far more strongly nucleophilic, ionised hydroxyl groups

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(Cell-$O^-$; aka *cellulosate anions*) within the substrate. Unfortunately, the alkali-induced generation of the strongly nucleophilic, ionised hydroxyl groups within the substrate not only favour covalent bond formation with the fibre but also promote undesirable alkali-induced hydrolysis of the reactive dye, which results in all commercial types of reactive dye displaying intrinsically low levels of dye-fibre fixation efficiency, of the order 60-80%. Furthermore, because dye hydrolysis and dye-fibre fixation occur simultaneously during immersion dyeing, and the presence of any unfixed dye in the final dyeing will result in inferior wet fastness, reactive dyeings must be subjected to an additional wash-off treatment to remove all traces of un-reacted and/or non-reactive dye from the dyed material. Hence, the immersion dyeing of cellulosic fibres using reactive dyes is a two-stage process in which the dye is firstly applied under aqueous alkaline conditions to promote dye-fibre fixation (the dyeing stage) and the dyed material is then subjected to a thorough, aqueous treatment to remove all unfixed dye (the wash-off stage).

Owing to the essential structural similariity of reactive dyes and direct dyes, the adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner analogous to that of direct dyes (7); furthermore, the mechanism by which added inorganic electrolyte promotes reactive dye uptake prior to dye-fibre fixation is also assumed to be analogous to that described for direct dye uptake (7). In order to secure satisfactory levels of dye uptake inorganic electrolyte, in the form of either NaCl or $Na_2SO_4$, must be added to the aqueous dyebath in the cases of both direct dyes and reactive dyes; in the case of reactive dyes, the added electrolyte also promotes the extent of covalent fixation of the dye to the substrate (ie dye-fibre fixation). Indeed, the immersion application of reactive dyes to cellulosic fibres is carried out typically in the presence of large amounts of $Na_2SO_4$ or NaCl, with upto 100 $gl^{-1}$ in the case of dark shades. From the perspective of the size of both the environmental and economic costs associated with the use of reactive dyes in cellulosic fibre dyeing, it has been estimated (6) that in 2015, some 6,000,000 T of added inorganic electrolyte may have been consumed in exhaust dyeing. Both the dyeing stage and subsequent wash-off stage in reactive dyeing generate copious amounts of wastewater that contains residual hydrolysed dye,

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unreacted dye, and very high levels of inorganic electrolyte, reactive dyeing wastewater typically presents considerable environmental and economic challenge.

## 3 proposed theory of the role of added electrolyte in the dyeing of cellulosic fibres using reactive dyes

As discussed (6), because the adsorption of reactive dyes onto cellulosic fibres in the absence of dye-fibre reaction is assumed to parallel that of direct dyes, the mechanism by which the dyes are adsorbed is also presumed to resemble that of direct dyes; consequently, the same theories which have been proposed to explain the promotional effect imparted by added inorganic electrolyte on the uptake of direct dyes are assumed to apply in the case of reactive dyes (6). Unfortunately, none of these theories satisfactorily explains why reactive dyes (or direct dyes) display low uptake when applied in the absence of added inorganic electrolyte nor can they account for the remarkable ability of added NaCl and $Na_2SO_4$ to promote the uptake of reactive dyes on cellulosic substrates.

From an analysis of published research findings relating to the influence of added inorganic electrolyte on reactive dye uptake, it was concluded (6) that the promotional effect imparted by inorganic electrolyte can be attributed to the marked proclivity of the dyes to aggregate in aqueous solution via coplanar association, a phenomenon that is encouraged not only by addition of inorganic electrolyte but also high dye concentration. It was therefore considered (6) that adding either NaCl or $Na_2SO_4$ to a reactive dye dyebath utilises the intrinsic propensity of reactive dyes to self-associate in solution via coplanar association, which is a consequence of the dye's characteristic long, planar structure and presence of one (or more usually) more sulfonate groups. As such, the outstanding ability of inorganic electrolyte to promote reactive dye aggregation in aqueous dyebaths can be attributed to the anionic charge on the dye anions derived from the $-SO_3^-$ groups being shielded by the added electrolyte counterions ($Na^+$), which reduces electrostatic repulsion between neighbouring dye anions so that hydrophobic interaction between planar aromatic rings in adjoining dye molecules are encouraged, which favours dye self-association. The shielding effect of the added inorganic electrolyte $Na^+$ counter-ions together with the strong π-π

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interactions between aromatic centres in neighbouring dye molecules will result in the dye molecules within the dye aggregates having lower aqueous solubility than their non-aggregated direct dye counterparts that are present in solution within the dyebath. As the driving force for dye-dye hydrophobic interaction is the need for the water molecules within the immediate proximity of the reactive molecules to reduce their contact with the dye solutes, so that disruption of the surrounding water structure by the dye molecules is minimised, the ensuing aggregates will therefore tend to coalesce and form low solubility dye particles that will be present within the dyebath in the form of a dispersion.

Hence, the addition of NaCl or $Na_2SO_4$ to an aqueous solution of a reactive dye reduces the solubility of the dye, as has been observed (8, 9); since this reduction in dye solubility increases with increasing amount of inorganic electrolyte (9, 10) the extent of electrolyte-induced dye aggregation also increases with increasing amount of added NaCl or $Na_2SO_4$, as has also been observed (11). It follows therefore that when sufficiently high amounts of added electrolyte are added to a reactive dye solution, the resulting reduction in dye solubility is likely to be so pronounced as to result in dye precipitation, especially when low liquor ratios are employed for dyeing, as again has been observed and will be reported in the next part of the paper. It was therefore suggested (6) that applying reactive dyes to cellulosic fibres in the presence of added inorganic electrolyte constitutes a process of controlled dye precipitation onto the substrate, in which sufficient added electrolyte is employed to induce the formation of a dispersion of dye particles in the aqueous dyebath without imparting flocculation of the dye.

### *3.1 the role of dye solubility in reactive dye uptake*

As previously recounted (6), reactive dyes display characteristically high aqueous solubility, as exemplified by values of 70-100 $gl^{-1}$ @ 20°C (12), 60-120 $gl^{-1}$ at 25°C (13), 70 $gl^{-1}$ @ 20°C (14) and 50-100 $gl^{-1}$ @ 50°C (15). Because of this inherent high aqueous solubility, when a reactive dye is dissolved in an aqueous dyebath that does not contain added inorganic electrolyte, the dye will display an inherent predisposition to remain in the aqueous phase (ie the dyebath) rather than

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transfer to the fibre phase; consequently, when applied in the absence of added NaCl or $Na_2SO_4$, the extent of dye uptake onto the cellulosic substrate will be low. However, the above discussion indicates that when inorganic electrolyte is added to a reactive dye dyebath, the solubility of the dye is reduced (8-10) owing to enhanced dye self-association, which results in dye uptake onto the cellulosic fibre being promoted. It therefore appears that the promotional effect of added NaCl or $Na_2SO_4$ on reactive dye adsorption can be attributed to the intrinsic predisposition of the dye to favour the aqueous phase having been markedly reduced, so that transfer of the dye to the substrate is favoured and dye uptake therefore promoted. In essence, the characteristically high aqueous solubility of reactive dyes, which is commonly conferred by the presence of sulfonate groups in the dye molecules, is responsible for the inherently low substantivity displayed by the dyes towards cellulosic fibres in the absence of added electrolyte; such high dye solubility is also the reason why added inorganic electrolyte is so effective in promoting reactive dye uptake.

This particular argument was previously advanced to explain the promotional effect of added inorganic electrolyte on the uptake of direct dyes on cellulosic fibres (3). That a similar rationale might apply to both direct dyes and reactive dyes seems a reasonable proposition, when it is recalled that the adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner analogous to that of direct dyes and the mechanism by which added inorganic electrolyte promotes reactive dye uptake prior to dye-fibre fixation is also assumed to be analogous to that described for direct dye uptake (7).

In this context, it was proposed (3) that in the case of direct dyes, the solubility of the dye in the dyebath is crucially important in terms of dye-fibre substantivity. By way of brief explanation, dye-fibre substantivity reflects the attraction between a dye and a fibre that results from intrinsic physical and chemical dye-fibre interactions that encourage the dye molecules to move from the aqueous dyebath to the solid fibre. Such dye-fibre interactions are countered by dye-water interactions that encourage the dye to remain within the aqueous dyebath and which resist dye-fibre substantivity. Therefore, in essence, the extent of direct dye transfer from a dyebath to a cellulosic fibre depends

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on the relative partition of the dye molecule between the aqueous dyebath (solution) phase and the fibre (solid) phase, which, in turn, will depend upon the aqueous solubility of the dye. Furthermore, it was proposed (3) that the solubility of a direct dye will also be a major contributory factor in the process of dye diffusion whereby dye molecules spontaneously move from the dyebath phase to the fibre phase as a result of the concentration gradient that exists between the two phases, since the solubility of the dye will impact directly on the magnitude of the dye concentration gradient. Hence, the most important aspect of an immersion dyeing process using direct dyes is the aqueous solubility of the dye since it determines the tendency of the dye to favour either the dyebath phase or the fibre phase and, thus, regulates the extent of dye transfer to the substrate.

An identical argument can be proposed in the case of reactive dyes since, as mentioned, they bear a close structural resemblance to direct dyes and both the adsorption of reactive dyes on cellulosic fibres and the mechanism by which added inorganic electrolyte promotes reactive dye uptake prior to dye-fibre fixation, are assumed to be analogous to that described for direct dyes (7).

### *3.2 a model to explain the adsorption of reactive dyes on cellulosic fibres*

Two approaches can be used to derive a model that explains reactive dye uptake on cellulosic fibres in both the presence and absence of added inorganic electrolyte; as previously described in the case of direct dyes and cellulosic fibres (3), such a model can also explain the promotional effect of reduced liquor ratio on the immersion reactive dyeing system.

#### 3.2.1 the theory of interstitial water

The concept of interstitial water has been described in terms of the development of a dyeing processes (16) and wash-off processes (17-20) for various dye-fibre systems, as well as the mechanism by which direct dyes are adsorbed onto cellulosic fibres (3). The concept is based on the assumption that a very small proportion of the water that is employed in exhaust dyeing resides within the interstices of the fibrous substrate. The amount of interstitial water within the substrate,

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which corresponds to its moisture regain at 100% relative humidity (~0.22 l per kg$^{-1}$ of fibre in the case of cotton), is that required to saturate the textile substrate and impart the crucially important actions of fibre wetting and fibre swelling. In the context of the model of dye adsorption described below, the term interstitial water refers specifically to water which is adsorbed by the fibrous substrate and, from which, the transfer of dye molecules/ions from the dyebath phase to the fibre phase occurs (3). The remaining proportion of the water that is used in immersion dyeing processes (~0.78 l kg$^{-1}$ in the case of cotton) constitutes the bulk dyebath that surrounds the water-swollen fibre phase and provides functions such as agitation, heating, dye dissolution, etc. As such, the aqueous dyebath includes both interstitial water located within the swollen fibrous substrate as well as bulk dyebath water located without the textile substrate. Thus, dissolved dye molecules will be present within the interstitial dye solution in the fibre phase and, also, within the bulk dye solution in the dyebath phase. The transfer of dye molecules from the bulk dye solution in the dyebath phase to the solid fibre occurs via the interstitial dye solution within the fibre.

The concept of interstitial water in dyeing assumes (3) that in porous substrates, such as textile fibres, different types of sorbed water are present namely:

- free water, which displays properties analogous to those of pure water in terms of solvency and mobility;
- strongly bound water which is closely associated with the substrate and is immobile and, therefore displays considerably different properties to those of free water;
- weakly bound water.

Such a model of water sorption compliments electric double-layer theory (13) which is commonly utilised to describe the ionic environment within solutions of polar liquids, such as water, when they are in the close vicinity of a charged surface, such as a textile fibre. Interstitial water is considered to comprise the three types of sorbed water referred to above and, as such, according to the concept of interstitial water in dyeing, the aqueous, ionic environment within the fibre interstices will be much different to that within the surrounding bulk dyebath, owing to the presence of both immobile bound

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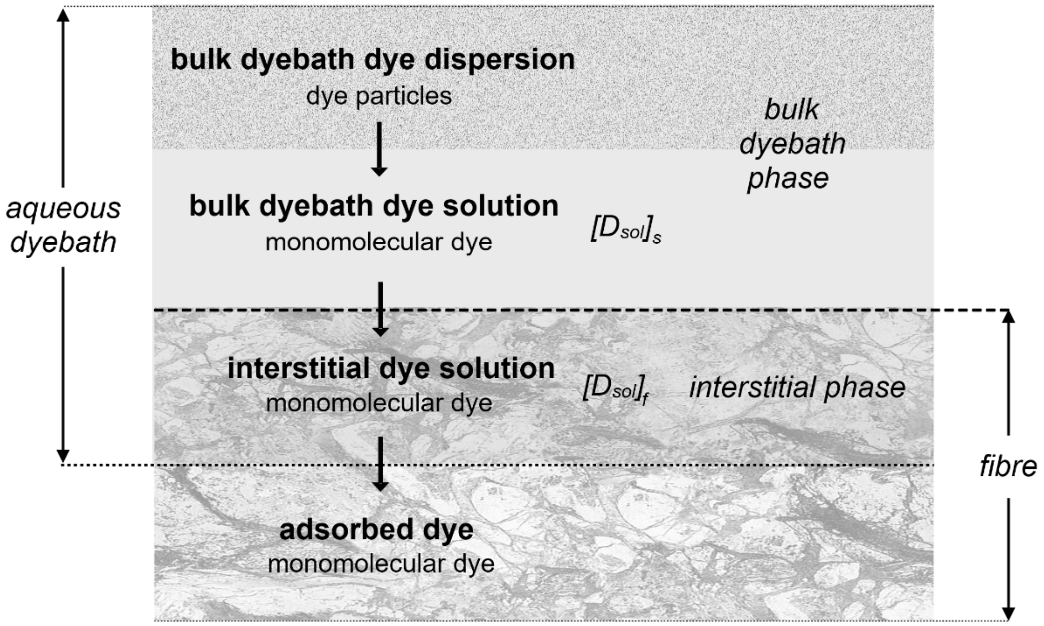
water molecules and reduced mobility bound water molecules within the interstitial regions of the substrate, as well as the influence of the charged cellulosic fibre surface on the distribution of nearby sorbed ions/molecules (3). Therefore, the behaviour of dye molecules that are present within the interstitial water in the fibre differs to that of dye molecules that reside within the bulk aqueous dyebath that surrounds the fibre. A later part of the paper will provide a detailed account of interstitial theory of dyeing in the context of various dye-fibre systems.

The wetted, swollen fibre therefore comprises an interstitial dye solution that is in intimate contact with dye solution that comprises the bulk dyebath which surrounds the fibre. It is considered that dyeing, or more correctly, the transfer of dye molecules from the aqueous phase (dyebath) to the fibre phase occurs from within this interstitial dye solution. Therefore, the aqueous dyebath comprises both interstitial water that resides within the swollen fibre as well as bulk dyebath water that is external to the textile substrate. Dissolved dye molecules are thus envisaged as being present within the interstitial dye solution in the fibre phase and within the bulk dye solution in the dyebath phase.

In the case of the manner by which direct dyes are adsorbed on cellulosic fibres, such a situation was represented by Scheme 1, in which the aqueous dyebath comprises both an interstitial phase and a bulk dyebath phase (3). The transfer of dye molecules from the bulk dye solution in the dyebath phase to the solid fibre occurs via the interstitial dye solution within the fibre.



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scheme 1 representation of direct dyeing mechanism (3)

Owing to the propensity of direct dye molecules to self-associate in solution, which is encouraged by the presence of added inorganic electrolyte, at the start of dyeing, a proportion of the dye will likely be present in the form of particles (ie aggregates of dye molecules) that will comprise a bulk dyebath dye dispersion within the bulk dyebath phase. Dissolved dye molecules/ions will also be present that make up a bulk dyebath dye solution; dissolved dye molecules will also populate the interstitial dye solution within the interstitial phase in the fibre. As dye aggregation decreases with increasing temperature, as dyeing proceeds, and the dyebath temperature increases, so the proportion of dye aggregates will reduce because dye molecules are released from the dye particles within the bulk dyebath dispersion and dissolve in the bulk dyebath solution; consequently, the proportion of dissolved dye ions within the dye solution in the dyebath will increase. Dye molecules that are present in the interstitial dye solution within the fibre will interact with the fibre and become adsorbed (for example, by means of a Freundlich-type or Langmuir-type process (2, 3)). As dye molecules are adsorbed onto the substrate, further dye molecules in the bulk dyebath solution transfer to, and replenish, the interstitial dye solution so that further dye adsorption can occur. Further dye molecules from the dye particles within the bulk dyebath dye dispersion are then released and dissolve in, and replenish, the bulk dyebath dye solution.

This process of dye dissolution from the bulk dyebath dye dispersion to the bulk dyebath dye solution, and the transfer of dye molecules/ions from the bulk dyebath dye solution to the interstitial dye solution, followed by dye molecule adsorption from the interstitial dye solution (as depicted by Scheme 1) continues until either all of the dye has been adsorbed or the fibre is saturated with dye.

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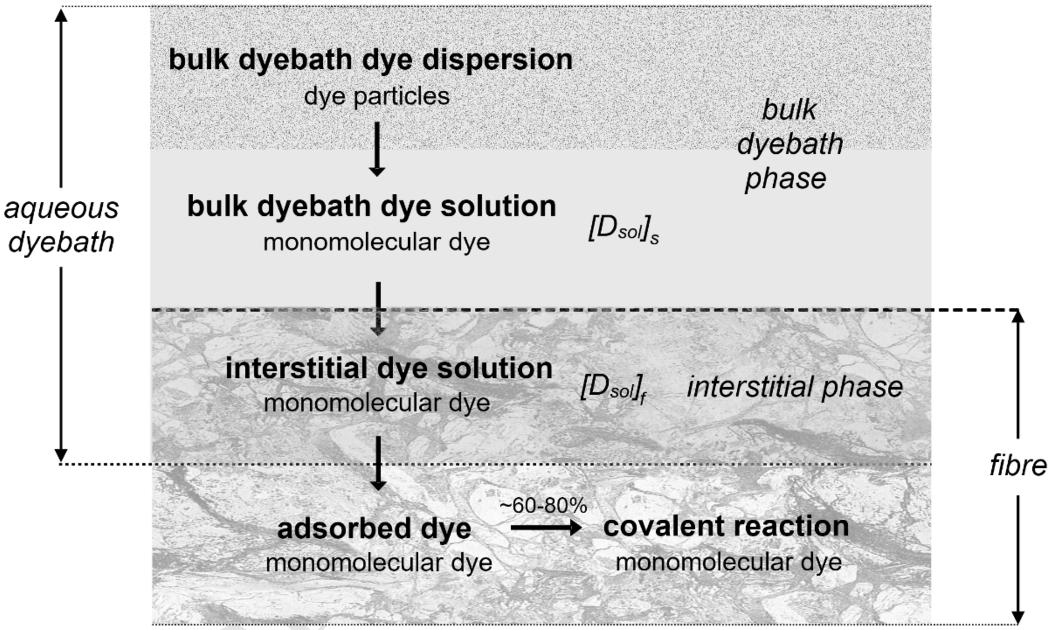
Because of the close structural resemblance of reactive dyes to direct dyes (ie both dye types are characteristically, long, planar, anionic molecules solubilised by one or more ionised sulfonate groups) (6), coupled with the fact that prior to the reactive dye forming a covalent reaction with the cellulosic fibre, the adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner analogous to that of direct dyes, the mechanism by which added inorganic electrolyte promotes reactive dye uptake prior to dye-fibre fixation can be described in terms of the notion that dye adsorption proceeds from interstitial dye solution present within the substrate, as previously described for direct dye uptake (2, 3), displayed in Scheme 1.



Scheme 2 representation of reactive dyeing mechanism

However, in the case of reactive dyes, as the adsorption of dye molecules onto the fibre from the interstitial dye solution can result in covalent bond formation with ionised hydroxyl groups in the substrate, Scheme 1 can be modified to include this (highly important) dye-fibre fixation stage of the dyeing process (Scheme 2). The inherent inefficiency of dye-fibre fixation displayed by reactive dyes on cellulosic fibres, which means that as much as ~30-50% of the dye applied can be present in the dyed substrate in the form of hydrolysed dye or unreacted dye, is reflected in Scheme 2.

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### 3.2.2 the use of two equations to describe reactive dye adsorption

It was intended that the theoretical model of reactive dye adsorption depicted above should be applicable to immersion dyeing processes in which dyeing had been carried out to equilibrium, as well as dyeing processes in which equilibrium dye adsorption had not been achieved. To this end, two approaches were employed to derive an equation which interpreted the above model of dye adsorption namely:

i. one that describes the distribution of dye between the two phases at any point throughout the immersion dyeing process;
ii. one that describes the effect of added NaCl or $Na_2SO_4$ on the distribution of the dye between the fibre and dyebath phases at the end of an immersion dyeing process, irrespective of whether or not equilibrium dye uptake had been achieved;

#### *3.2.1.1 an equation that applies to dye uptake during immersion dyeing*

To achieve complete dye exhaustion in immersion dyeing, the inherent tendency of dissolved reactive dye molecules to move from the dyebath phase to the fibre phase under the influence of the process of diffusion, that is driven by the dye concentration gradient between the dye in the dyebath phase and the fibre phase, must be supplemented by dye-fibre substantivity. As mentioned (6), the degree of substantivity displayed by a given reactive dye towards a particular cellulosic textile fibre can be controlled by adjusting dyebath conditions (eg dyeing auxiliaries, controlling the rate of temperature rise, etc.). As these adjustments principally regulate the solubility of the dye in the aqueous dyebath, the primary contributor to reactive dye-cellulosic fibre substantivity and, consequently, the predisposition of the dye to favour the fibre phase or dyebath phase, can be assumed to be the solubility of the dye in the dyebath, as proposed in the case of direct dyes (3). Hence, Eq 1, which was devised for direct dyes (3), can be used to relate dye-fibre substantivity to dye solubility, in which *[D]*, the total amount of dye present within an immersion reactive dyeing

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system comprises dye that is present in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$ as well as dye that is present within the bulk dyebath dye solution in the dyebath phase, $[D_{sol}]_s$. Eq 1 was used to show that the intrinsic low substantivity displayed by direct dyes towards cellulosic fibres in the absence of added electrolyte is a consequence of the dye's high aqueous solubility and the ensuing preference of the dye to remain within the aqueous dyebath phase (3); a similar situation can be assumed to apply in the case of reactive dyes.

$$S = \frac{[D_{sol}]_f}{[D_{sol}]_s} = \left(\frac{[D] - [D_{sol}]_s}{[D_{sol}]_s}\right) \qquad 1$$

Since the ratio $[D_{sol}]_f/[D_{sol}]_s$ in Eq 1 describes the relative partition of the dye between the fibre phase and the solution phase; the higher the value of this ratio the greater is the distribution of the dye in favour of the fibre phase (ie $[D_{sol}]_f > [D_{sol}]_s$) and, therefore, the greater is the extent of dye uptake. The ratio $[D_{sol}]_f/[D_{sol}]_s$ therefore represents the degree of substantivity displayed by the reactive dye towards the cellulosic fibre at a given stage in the immersion dyeing process, and so $S$ is the *substantivity coefficient* of the dye at a given point in the dyeing process.

Owing to the term ($[D]$ - $[D_{sol}]_s/[D_{sol}]_s$) in Eq 1, the degree of substantivity displayed by the dye towards the fibre, as reflected by the substantivity coefficient, $S$, will be determined by the amount of dye in the bulk dyebath dye solution, $[D_{sol}]_s$ relative to the total amount of dye within the dyeing system, $[D]$; the greater this difference, the higher will be dye-fibre substantivity, and, therefore, the greater the extent of dye uptake. Eq 1 therefore provides a model that relates both the degree of reactive dye-cellulosic fibre substantivity, via $S$, and the corresponding extent of dye uptake achieved, to the solubility of the dye: thus, Eq 1 provides an explanation for the nature of reactive dye-cellulosic fibre substantivity based on the role of dye solubility.

Since, according to the concept of interstitial water in dyeing, in Eq 1, the transfer of dye from the bulk dyebath dye solution, $[D_{sol}]_s$, to the interstitial dye solution, $[D_{sol}]_f$, as well as the total amount of

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dye in the immersion dyeing system, $[D]$, are both expressed in terms of mass per unit volume (eg g $l^{-1}$), because of the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$, the substantivity coefficient $S$ also has dimensions of mass per unit volume (eg $gl^{-1}$). Such a situation seems reasonable when it is recalled that substantivity coefficient, $S$, describes the tendency of the reactive dye to favour adsorption onto the substrate and, according to the concept of interstitial water in dyeing, the adsorbed dye is assumed to reside within the dye solution that is present in the interstitial phase within the fibre (ie $[D_{sol}]_f$).

Eq 1 predicts that the partition of the reactive dye between the fibre and dyebath phases during dye adsorption depends on the concentration of the dye within the bulk dyebath solution phase, $[D_{sol}]_s$. The addition of inorganic electrolyte to an aqueous reactive dye dyebath can therefore be considered as a dilution effect, because the solubility of the dye is reduced as a result of electrolyte-induced dye aggregation, which leads to a lower amount of dye in solution in the dyebath phase. According to Eq 1, the driving force for the transfer of reactive dye molecules from the dyebath phase to the fibre phase is expressed by the concentration gradient, $[D_{sol}]_f/[D_{sol}]_s$ that exists between the amount of dye in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$, and the amount of dye in the dye solution within the dyebath phase, $[D_{sol}]_s$. As dye solubility is reduced owing to dye aggregation, it follows that in the presence of added NaCl or $Na_2SO_4$, because $[D_{sol}]_s$ has been lowered, the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$ will increase and, therefore, the dye concentration gradient (ie $[D_{sol}]_f/[D_{sol}]_s$) must also increase, so that a higher driving force for dyeing will be established.

As such, Eq 1 explains that the partition of the dye between the fibre and solution phases, $[D_{sol}]_f/[D_{sol}]_s$ (ie $S$) increases in the presence of added NaCl or $Na_2SO_4$ because the amount of dye in the dye solution within the bulk dyebath, $[D_{sol}]_s$, is lowered and, therefore, the amount of dye in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$, increases correspondingly. In effect, the application of reactive dyes to cellulosic fibres in the presence of added inorganic electrolyte is really a process of controlled precipitation of the dye within the fibre.

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However, Eq 1 describes the likely partition of the dye between the interstitial dye solution within the fibre phase and the bulk dye solution in the dyebath phase only in terms of the solubility of the dye. It therefore does not take into account the involvement of other dyebath variables that can be expected to participate in dye-fibre substantivity (eg temperature, dyebath-fibre interchange rate, etc.). Thus, when using Eq 5, the value of the ratio $[D_{sol}]_f / [D_{sol}]_s$ is indicative only, insofar as, a low value of $[D_{sol}]_f / [D_{sol}]_s$ implies that high dye solubility in the dyebath demotes dye uptake whereas a high value of $[D_{sol}]_f / [D_{sol}]_s$ suggests that reduced dye solubility in the dyebath encourages dye uptake.

The promotion of reactive dye uptake onto cellulosic fibres imparted by added inorganic electrolyte can therefore be explained in terms of the model proposed for direct dyes on cellulosic fibres, (3), namely, the combined effects of increased dye aggregation and reduced dye solubility on the effective concentration of dye in the aqueous dye solution in the dyebath phase. Hence, the amount of dye in the fibre solution phase (ie the fibre) is determined by the effect of the added inorganic electrolyte on the concentration of reactive dye in the dyebath solution phase (ie the dyebath).

As discussed in section 4, this mechanism can also be used to describe the promotional effect of reducing liquor ratio on the uptake of reactive dyes on cellulosic fibres in both the presence and absence of added electrolyte.

#### *3.2.1.2 an equation that applies to the final dye distribution at the end of dyeing*

In terms of the mechanism by which reactive dyes are adsorbed on cellulosic fibres, Eq 2 is widely accepted as describing the partition of dye between the fibre phase and the solution phase when equilibrium dye uptake has been attained (ie when dye adsorption and dye desorption processes are equal) (7). In Eq 2, $[D]_f$ is the amount of dye present in the fibre phase (ie the substrate) relative to the amount of fibre and $[D]_s$ is the amount of dye in solution (ie the dyebath) relative to the amount of solution. The distribution of the dye between the dyebath, *s* and fibre, *f*, phases is

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described by the partition coefficient, $K$; the higher the value of $K$ the greater is the partition of the dye in favour of the fibre phase (ie $[D]_f > [D]_s$) and the greater is dye uptake.

$$K = \frac{[D]_f}{[D]_s} \qquad 2$$

Equations based on Eq 2 are commonly used to calculate the thermodynamic standard affinity of reactive dyes on cellulosic substrates, $-\Delta\mu^{\theta}$, taking into account the effect of alkali on the extent of ionisation of the hydroxyl groups in the fibre (7). Eq 2 (and equations based upon it) therefore only relates to the final distribution of dye between the fibre and dyebath phases (ie that achieved at the end of an immersion dyeing process).

The analysis of equilibrium dye adsorption data using variants of Eq 2 is widely used as a means of interpreting the mechanism by which reactive dye adsorption has occurred (in the absence of dye-fibre reaction) in a manner analogous to that of direct dyes (7) and, therefore, is considered to provide information about how reactive dye (and direct dye) molecules interact with the textile substrate, for example, via specific site interactions (Langmuir-type) or non-specific site interactions (Freundlich-type). However, the use of Eq 2 and variants to analyse isothermal equilibrium dye adsorption data provides no information regarding the dyeing process prior to equilibrium, which, from the viewpoint of a commercial immersion dyeing processes that are not carried out to equilibrium, is a very important consideration. Also, equations such as Eq 2 (and others) are unable to satisfactorily explain not only why reactive dyes display inherently low substantivity towards cotton and other cellulosic fibres in the absence of added inorganic electrolyte but also why added inorganic electrolyte (or reduced liquor ratio) so effectively promote dye uptake.

Eq 1 was therefore derived to address these issues in the case of direct dyes and cellulosic fibres (3). In this context, whilst Eq 2 (and derivatives) offers information regarding the relative partition of

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a dye between the fibre and dyebath phases at the end of dyeing, Eq 1 provides information about how that partition may have been achieved.

It has been demonstrated (3) that, if dye solubility is assumed to be the major contributor to reactive dye-fibre substantivity and, also, that the solubility of the reactive dye in the dyebath phase governs the partition of the dye between the fibre and dyebath phases, the relationship represented by Eq 2 can be used to interpret the effect of electrolyte-induced aggregation and consequent reduced solubility on the extent of direct dye at the end of an immersion dyeing process. Such a situation applies in the case of dyeings which have not been carried out to equilibrium (3), since, in terms of the work described in this part of the paper (and others that follow), the mechanism of reactive dyeing from the viewpoint of dye-fibre interactions (prior to dye fixation), as normally revealed from analysis of equilibrium dyeings using derivatives of Eq 2, is not sought. Instead, the aims of the work undertaken were to firstly establish the motivational force that encourages the transfer of the reactive dye molecules from the dyebath phase to the fibre phase and, secondly, to clarify the roles of added inorganic electrolyte and reduced liquor ratio in this dye transfer process, under conditions that mimic commercial dyeing (ie non-equilibrium) dyeing.

To this end, Eq 3 was derived (3) to explain the effect of added inorganic electrolyte on direct dye adsorption, in which the total amount of dye within the reactive dyeing system, *[D]*, comprises dye that is present in both the fibre phase, $[D]_f$ and the dyebath phase, $[D]_s$.

$$K = \frac{[D]_f}{[D]_s} = \left(\frac{[D]-[D]_s}{[D]_s}\right) \qquad 3$$

Therefore, the distribution of the reactive dye in solution between the fibre, $[D]_f$, and dyebath, $[D]_s$, phases at the end of an immersion dyeing process is determined by the concentration of dye in solution in the dyebath, $[D]_s$. The higher the value of this ratio (ie $[D]_f$ / $[D]_s$) then the greater the partition of the dye in favour of the fibre phase (ie $[D]_f > [D]_s$) and, therefore, the greater is the extent

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of dye uptake onto the substrate. Eq 3 shows the marked dependency of final dye uptake (ie $[D]_f/[D]_s$) and thus partition coefficient, $K$, on the solubility of the reactive dye in the dyebath, $[D]_s$. The similarity between Eq 3 and Eq 1 is obvious.

According to Eq 3, when dyeing is undertaken in the presence of added $Na_2SO_4$ or NaCl, the solubility of the reactive dye is reduced because of electrolyte-induced aggregation, so that the effective concentration of dye in the dyebath (ie $[D]_s$) will be lowered. As the driving force for dyeing (ie the transfer of dye molecules from the aqueous phase (dyebath) to the solid phase (fibre)), is the concentration gradient, $[D]_f/[D]_s$, between the amount of dye in the dyebath, $[D]_s$, and fibre,$[D]_f$, phases, then because the effective concentration of dye in the dyebath (ie $[D]_s$) is lowered in the presence of added NaCl or $Na_2SO_4$, then the term ($[D] - [D]_s/[D]_s$) will increase and, therefore, the dye concentration gradient (ie $[D]_f/[D]_s$) will also increase, so that a higher driving force for dyeing is developed.

Thus, Eq 3 predicts, as does Eq 1, that the amount of dye that is adsorbed by the substrate is determined by the amount of dye in solution, which is depends upon the solubility of the dye in the aqueous dye solution within the dyebath phase.

#### *3.2.1.3 comparison of the two equations*

Whilst Eq 1 and Eq 3 both describe the promotional effect imparted by added inorganic electrolyte on reactive dye adsorption, the equations differ in terms of the nature of the data that is required for their solution, because the two equations apply to different stage of the immersion dyeing process. Eq 1 concerns the manner by which the reactive dye molecules transfer from the dyebath phase to the fibre phase during the dye adsorption process (ie during dyeing), which therefore requires information about the aqueous solubility of the dye in both the interstitial dye solution and the bulk dyebath solution. Such data is not especially easy to collect: for example, in the case of non-isothermal dyeing processes, the collection of data of this type would involve determining dye solubility as a function of temperature and ionic environment, because dyebath temperature varies

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during dyeing and the dissociation of alkalis that are employed in reactive dyeing, such as $NaHCO_3$, varies as a function of temperature. Because Eq 3 describes how the particular final distribution of the reactive dye molecules between the dyebath and fibre phases was achieved at the end of the dye adsorption process (ie at the end of dyeing) for which knowledge of the far more easily experimentally measurable amounts of dye in the solid fibre and the dyebath at the end of dyeing are requires; thus Eq 3 offers a more amenable alternative to Eq 1.

## 4 the role of liquor ratio in the dyeing of cellulosic fibres using reactive dyes

The general effects of liquor ratio on immersion dyeing processes was discussed in the first part of the paper (1). In essence, the liquor ratio selected for reactive dyeing has a marked effect on the rate and extent of dye uptake as well as the degree of dye-fibre fixation achieved. Liquor ratio also influences the degree of substantivity displayed by the dye towards the fibre because the amount of water in the dyebath available for dye dissolution and, thus, the amount of dye available for adsorption, is determined by liquor ratio. Also, because the amount of dye used in dyeing is normally based on the mass of fibre (ie % omf), the effective dye concentration in the dyebath is also determined by liquor ratio. Hence, the intensity of the dye/inorganic electrolyte interactions that are responsible for promoting dye uptake are influenced greatly by liquor ratio.

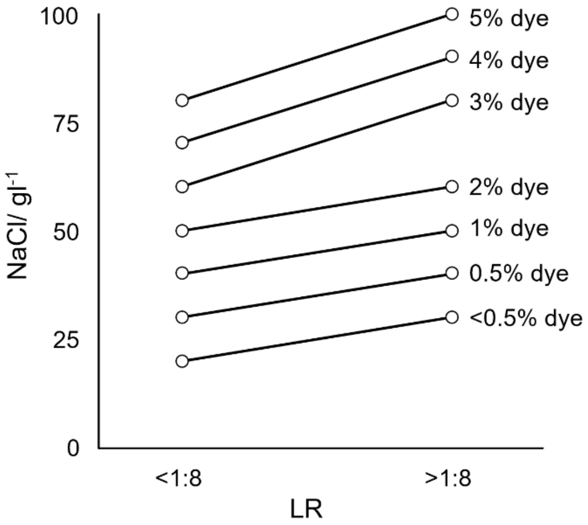

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Figure 1 effect of liquor ratio on amount of NaCl required for application of *Novacron FN* dyes; plotted using data from (8)

Whilst the characteristically high aqueous solubility of reactive dyes is beneficial in terms of the renowned ability of the dyes to respond in a controlled and predictable manner to added NaCl or $Na_2SO_4$ during exhaust dyeing, the solubility of the dye in the aqueous dyebath, as reflected by the liquor ratio used for dyeing, impacts directly on the effectiveness with which added electrolyte promotes dye uptake. This is illustrated graphically by the data displayed in Figure 1 which shows that the amount of added NaCl required for the application of *Novacron FN* (Huntsman) reactive dyes increases with increase in liquor ratio as a function of the amount of dye applied (8). The greater amounts of electrolyte required for dyeing when 3-5% omf dye is used at liquor ratios >1:8 are, presumably, to offset the comparatively higher levels of dye solubility at such long liquor ratios.

Several workers have sought to examine the effect of liquor ratio on reactive dye uptake [eg (21-24), as exemplified by Gorensek *et al* (25) who found that reducing liquor ratio increased both the extent of dye uptake and fixation of four commercial monochlorotriazinyl reactive dyes on cotton, the observed increase in uptake at lower liquor ratios being attributed to increased dye-fibre substantivity (24). Whilst the promotional effect that a reduction in liquor ratio imparts to dye uptake in immersion dyeing processes is a well-discussed topic, the precise nature by which this promotional effect might be achieved has not been fully resolved.

### *4.1 proposed theory of the role of liquor ratio in the dyeing of cellulosic fibres using reactive dyes*

Two approaches can be used to derive a model that explains why reducing the liquor ratio used for dyeing increases the uptake of reactive dyes on cellulosic fibres, in both the presence and absence of added inorganic electrolyte.

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### 4.1.1 an equation that applies to dye uptake during immersion dyeing

Recourse can be made to the model that describes the effect of reducing liquor ratio on the adsorption of direct dyes on cotton, which invokes the concept of interstitial water in dyeing (4). When the liquor ratio used for dyeing is lowered, it follows that the solubility of the reactive dye will be lowered, because the amount of water available for dissolution of the dye has reduced. Thus, in terms of Eq 1, as the amount of reactive dye in solution in the dyebath phase, $[D_{sol}]_s$, has been reduced then the term ($[D] - [D_{sol}]_s/[D_{sol}]_s$) will increase and, therefore, the dye concentration gradient (ie $[D_{sol}]_f/[D_{sol}]_s$) will also increase, so that a higher driving force for dyeing will be established.

In the case of direct dye adsorption (2), this effect was expressed by Eq 4, where $L$ is the fractional liquor ratio given by Eq 5, in which $m$ is the mass of fibre and $v$ the volume of dyebath used in dyeing (the units of $L$ are mass/volume, such as $gl^{-1}$); such a model can be used for reactive dyes.

As values of $L$ will increase with decreasing liquor ratio (eg $L = 0.01$ in the case of a 1:100 liquor ratio; L = 0.02 for a liquor ratio of 1:50; L = 0.1 for a 1:10 liquor ratio, etc.), the marked dependency of final dye uptake (ie $[D_{sol}]_f/[D_{sol}]_s$) and thus partition coefficient, $K$, on dye solubility in the dyebath, $[D_{sol}]_s$ described by Eq 1 is directly impacted by liquor ratio via the term $[D_{sol}]_s/L$ in Eq 4 (3).

$$K = \frac{[D_{sol}]_f}{\frac{[D_{sol}]_s}{L}} = \left( \frac{[D] - \frac{[D_{sol}]_s}{L}}{\frac{[D_{sol}]_s}{L}} \right) \qquad 4$$

$$L = \frac{m}{v} \qquad 5$$

Although liquor ratio, via $L$, has a direct impact upon the amount of dye in solution in the bulk dyebath phase, $[D_{sol}]_s$, liquor ratio will also have an indirect influence upon the amount of dye in the interstitial solution in the fibre, $[D_{sol}]_f$, because of the term ($[D_{sol}]_s/L$), in that as values of $[D_{sol}]_s$ decrease with decreasing liquor ratio (owing to increasing values of $L$), then values of $[D_{sol}]_f$ increase accordingly. As the solubility of the reactive dye in bulk dyebath dye solution, $[D_{sol}]_s$, is reduced when liquor ratio is lowered, it follows that term ($[D] - [D_{sol}]_s/[D_{sol}]_s$) will increase and, therefore, the dye concentration gradient (ie $[D_{sol}]_f/[D_{sol}]_s/L$) must also increase, so that a higher driving force for dyeing arises.

In effect, the increased uptake of reactive dyes that accompanies a reduction in the liquor ratio employed for dyeing is a process of controlled precipitation of the dye within the fibre. As such, reducing the liquor ratio used for dyeing is analogous to that of adding inorganic electrolyte to the dyebath, insofar as, both actions lower the concentration of dye in the dyebath solution phase.

It was shown (5), that Eq 4 explained why the use of very low liquor ratios enabled direct dyes to be applied in the complete absence of added NaCl or $Na_2SO_4$ because reducing the liquor ratio used for dyeing achieves the same outcome as adding inorganic electrolyte to the direct dye dyebath, namely promotion of dye uptake. Since, as discussed above, it is assumed that in the absence of dye-fibre reaction, the adsorption of reactive dyes on cellulosic fibres occurs in a manner analogous to that of direct dyes (7), then a similar situation should apply in the case reactive dye uptake on cotton.

### 4.1.2 an equation that relates to the final dye distribution at the end of dyeing

In the case of the model proposed for direct dyes on cellulosic fibres (4), the effect of liquor ratio on the final distribution of the dye between the fibre and dyebath phases at the end of an exhaust dyeing process can also be explained from a theoretical viewpoint in the context of the partition expressed by Eq 3. For this, Eq 6 was derived, where *L* is the fractional liquor ratio, as defined in Eq 5.

$$S = \frac{[D]_f}{\frac{[D]_s}{L}} = \left(\frac{[D] - \frac{[D]_s}{L}}{\frac{[D]_s}{L}}\right) \qquad 6$$

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The distinct dependency of final dye uptake (ie $[D]_f/[D]_s$) and thus the substantivity coefficient, $S$, on dye solubility in the dyebath, $[D]_s$ described by Eq 4 is directly influenced by liquor ratio via the term $[D]_s/L$ in Eq 6 (4) ; the same approach can be used to explain the effect of liquor ratio on reactive dye uptake.

Eq 6 therefore describes the relationship between the distribution of the reactive dye, at the end of dyeing, between the fibre, $[D]_f$, and solution, $[D]_s$, phases, expressed in terms of the substantivity coefficient, $S$, and fractional liquor ratio, $L$. Liquor ratio directly effects the amount of reactive dye in the dyebath rather than the amount of dye in the fibre insofar as, because of the term ($[D]_s/L$). As liquor ratio is lowered, the effective concentration of dye in the dyebath (ie $[D]_s$) is also lowered because of the term ($[D]_s/L$). It follows that the term ($[D] - [D]_s/[D]_s$) will therefore increase and the dye concentration gradient (ie $[D]_f/[D]_s$) will increase accordingly, so that a higher driving force for dyeing is developed.

From this it follows that it is the effect of liquor ratio on the amount of reactive dye in solution that influences the partition of the dye between the fibre and solution phases.

### 4.1.3 comparison of the two models

Eq 4 and Eq 6 provide reasonable explanations for the promotional effect imparted by reduced liquor ratio on reactive dye adsorption. For similar reasons to those recounted in section 3.2.1.3, the two equations differ in terms of the particular stages of the dyeing process to which they apply and the nature of the data that is required for their solution. Both models suggest that reactive dyeing should be achievable in the complete absence of added inorganic electrolyte using low liquor ratios.

This is a focus of the work described in the next part of the paper. The results of dyeings carried out on cotton produced using commercial grade reactive dyes at various liquor ratios in both the absence and presence of added NaCl are interpreted in terms of the above model of reactive dye uptake. It will be demonstrated that the effects of both added electrolyte and reduction in liquor ratio

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are sufficiently well described using the model to explain why it is possible to obtain dyeings using reactive dyes on cotton in the complete absence of added inorganic electrolyte.

## 5 conclusions

A model is proposed to account for the promotional effect imparted by added NaCl or $Na_2SO_4$ on the uptake of reactive dyes on cellulosic fibres, which utilises the concept of interstitial water. According to this model, which was based upon that previously developed for direct dyes on cellulosic fibres, adding inorganic electrolyte to a reactive dye dyebath promotes dye uptake because the electrolyte encourages dye aggregation in the dyebath, so that the inherent preference of the dye to favour the aqueous phase shifts towards the fibre phase, which results in increased dye uptake. It was shown that the same theoretical model could also explain the promotional effect which reducing the liquor ratio used for dyeing has on the uptake of reactive dyes on cellulosic fibres.

As such, the theoretical models describe both the motivational force that drives the transfer of the reactive dye molecules from the dyebath to the fibre as well as the important combinatorial nature of added inorganic electrolyte and liquor ratio in this transfer process, under conditions that represent commercial dyeing (ie non-equilibrium).

In the next part of the paper, the theoretical model will be interrogated by determining whether it can be used to interpret the results obtained for a series of dyeings on cotton which had been carried out using commercial grade direct dyes, employing different liquor ratios in both the absence and presence of added NaCl. Indeed, the next part of the paper will demonstrate how the theoretical models explain why it is possible to secure uniform dyeings of the desired depth of shade on cotton using commercial reactive dyes in the complete absence of added inorganic electrolyte.

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## Highlights

- the role of liquor ratio in reactive dye application is modelled
- interstitial water is used to show that low liquor ratio reduces dye solubility
- reducing liquor ratio promotes dye aggregation

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