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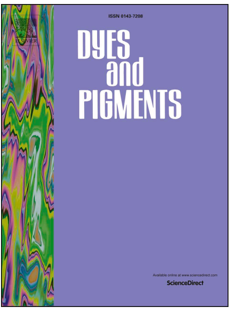

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The role of auxiliaries in the immersion dyeing of textile fibres: Part 5 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with direct dyes

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Abstract

Both the colour strength of 2% omf dyeings and the extent of dye exhaustion achieved for three commercial grade direct dyes on cotton were promoted by the addition of 20 gl^{-1} NaCl at each of eight liquor ratios (1:50, 1:20, 1:10, 1:6, 1:3, 1:2, 1:1.5 and 1:1). The extent of electrolyte-enhanced dye uptake decreased with decreasing liquor ratio. For each of the three dyes, unlevel dyeings were obtained at 1:1 liquor ratio only in the presence of added electrolyte, whereas level dyeings were secured even at 1:1 liquor ratio in the complete absence of added electrolyte. The depth of the dyeings obtained in the absence of added electrolyte using both 1:1 and 1:1.5 liquor ratios were of similar magnitude to those secured using 1:10, 1:20 and 1:50 liquor ratios in the presence of 20 gl^{-1} NaCl. The promotion of dye uptake imparted by both added electrolyte and reduced liquor ratio were interpreted in terms of their effects on the substantivity of the direct dyes towards the cotton substrate. It is proposed that adding electrolyte to the dyebath and reducing the liquor ratio employed for dyeing have the same consequence in terms of enhancing dye uptake, namely that of encouraging dye aggregation in the dyebath which reduces the aqueous solubility of the anionic dye, which, in turn, results in the inherent preference of the dye to favour the aqueous phase shifting towards the fibre phase.

Highlights

- the role of inorganic electrolyte in direct dyeing is investigated experimentally
- added electrolyte reduces dye solubility and increases dye aggregation
- use of low liquor ratio enables dyeing in the absence of added electrolyte

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

1 Introduction

This paper concerns the role of some of the common auxiliaries that are employed in the application of dyes to textile fibres using immersion (exhaust) dyeing processes. Despite their widespread commercial usage, the precise mode of action of many dyeing auxiliaries has not been fully resolved. In the first part of the paper (1), the different types of auxiliary that are commonly used in exhaust dyeing processes were discussed, together with the nature of the assistance that such auxiliaries were intended to impart to immersion dyeing processes were discussed. In addition, both environmental and financial aspects associated with the use of such auxiliaries, as well as the relationship between liquor ratio and auxiliary utilisation, were considered (1). The second part of the paper (2) presented an analysis of the various theories which have been proposed to describe the manner by which the most important auxiliary utilised in the dyeing of cellulosic fibres using direct dyes, namely inorganic electrolyte in the guise of either sodium sulfate or sodium chloride, promotes the uptake of direct dyes. As conventional theoretical descriptions of the mechanism of direct dye adsorption do not satisfactorily account for the inherently low uptake on cellulosic fibres displayed by direct dyes in the absence of added inorganic electrolyte, nor why NaCl or Na_2SO_4 are so effective in promoting dye uptake, a theoretical model was proposed, based on the concept of interstitial water, to explain the promotional effect of added inorganic electrolyte on the uptake of direct dyes on cellulosic fibres (3).

According to this theoretical model, the characteristically low substantivity of direct dyes towards cellulosic fibres when applied in the absence of added inorganic electrolyte can be attributed to the dye's high aqueous solubility and corresponding preference to remain within the aqueous dyebath phase rather than to transfer to the solid fibre phase. Adding NaCl or Na_2SO_4 to a direct dye dyebath encourages dye aggregation which reduces the solubility of the dye in the dyebath phase, so that the inherent predilection of the previously highly soluble dye to favour the aqueous phase shifts towards the fibre phase and, therefore, dye uptake is promoted. Two equations were derived to interpret this theoretical model of direct dye adsorption; whilst each equation invoked the concept of interstitial water in dyeing, they differed in terms of both the particular stages of the immersion dyeing process to which they apply and the type of data that is required for their solution.

It was subsequently demonstrated (4) that the same theoretical model could be used to explain the promotional effect that is imparted to direct dye uptake by a reduction in the liquor ratio employed for dyeing and two equations were derived to interpret this theoretical model. It was concluded (4) that because adding inorganic electrolyte to a direct dye dyebath and reducing the liquor ratio used for dyeing achieve the same outcome, namely the promotion of dye uptake, it should be 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.

This is the focus of the work described in this part of the paper. Results are presented of dyeings on cotton that were undertaken using commercial grade direct dyes, in which the liquor ratio employed for dyeing was varied over a wide range and dyeing was carried out in both the absence and presence of a constant concentration of added NaCl. The results of these practical dyeings are interpreted in terms of the theoretical model of direct dye uptake (3, 4), according to which, the effects of both added inorganic electrolyte and reduction in liquor ratio can be explained in terms of the combined effects which increased dye aggregation and reduced dye solubility have upon shifting the predisposition of the dye to favour the fibre phase rather than the aqueous dyebath phase. Subsequent parts of the paper will consider the role of auxiliaries that are utilised in the application of reactive dyes to cellulosic fibres as well as other classes of dye to other types of textile substrate.

1.1 direct dyes

By way of brief introduction, direct dyes currently enjoy an ~11% share of global dye usage on cellulosic fibres, corresponding to an estimated global usage of some 56,000 - 57,000 T in 2015 (2). The exhaust application of direct dyes to cellulosic fibres requires the addition of inorganic electrolyte, in the form of either NaCl or Na_2SO_4, to the aqueous dyebath in order to promote dye uptake and achieve the desired depth of shade. As recounted (1), such usage of added inorganic electrolyte presents major economic problems, not only directly, because of the cost of the very large amounts of NaCl or Na_2SO_4 that are routinely consumed in dyeing, but also due to the considerable costs incurred in treating the extremely large amounts of environmentally-challenged, saline wastewater that are generated. Indeed, it has been estimated that as the exhaust application of direct dyes to cellulosic fibres is typically carried out in the presence of between 5 gl^{-1} and 20 gl^{-1} added NaCl or Na_2SO_4, then between ~112,00 and 540,000 T of added inorganic electrolyte may have been used in the exhaust dyeing of cellulosic fibres with direct dyes in 2015 (2).

Clearly, if it were possible to dye cellulosic fibres using direct dyes in the absence of added electrolyte, substantial environmental advantages and economic rewards should be achievable.

1.2 the role of added electrolyte in the dyeing of cellulosic fibres using direct dyes

The use of added electrolyte to promote the uptake of direct dyes onto cotton (and other cellulosic fibres) stems from the discovery, in 1883 by Böttiger, that a novel, red azo dye, which was marketed in the following year under the trade name *Congo Red,* could be applied to cotton in the presence of added electrolyte. As such, *Congo Red* became the first member of the currently very large dye class known in the Colour Index as *direct dyes* (5, 6), namely C.I. Direct Red 28. Characteristically, on cellulosic fibres, direct dyes furnish low-cost, bright dyeings of moderate/good light fastness and poor/moderate wet fastness.

As mentioned, from a consideration of the manifold theories that have been proposed over many decades to describe the role of added inorganic electrolyte in the immersion dyeing of cellulosic fibres with direct dyes, it was concluded (2, 3) that the promotional effect imparted by added NaCl or Na_2SO_4 on dye uptake can be attributed to the marked propensity of direct dyes to aggregate in aqueous solution via coplanar association and the facts that this particular characteristic of direct dyes in aqueous solution is encouraged at both high dye concentrations and the addition of electrolyte. In essence, the characteristically high aqueous solubility of direct dyes, which is commonly conferred by the presence of sulfonate groups, is responsible for the inherently low substantivity displayed by direct 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 dye uptake (3). From the viewpoint of immersion dyeing, the high aqueous solubility of direct dyes means that when dissolved in the dyebath in the absence of added electrolyte, the dyes display an innate tendency to remain in the aqueous dyebath, rather than transfer to the fibre phase; thus, in the absence of added electrolyte, the extent of dye uptake is low. In this context, the aqueous solubility of commercial direct dyes, which ranges from ~5-200 gl^{-1} at $98^{o}C$, increases with increasing temperature (7) and pH (8), but has been shown to be markedly reduced in the presence of inorganic electrolyte (9).

Adding either NaCl or Na_2SO_4 to a direct dye dyebath exploits the inherent tendency of direct dyes to aggregate in solution via coplanar association, which stems from the dye's distinctive architecture, namely their characteristically long, linear structure and presence of one (or more usually) more sulfonate groups which impart both water solubility and anionicity. Indeed, the remarkable ability of NaCl and Na_2SO_4 to induce direct dye self-association in aqueous dyebaths stems from the electrolyte counterions (Na^+) screening the anionic charge on the dye anions (ie derived from $-SO_3^-$ groups) which expedites hydrophobic interaction between planar aromatic regions in neighbouring dye molecules. The driving force for this hydrophobic interaction is the necessity of the water molecules that surround the dye molecules to reduce their interaction with the direct dye solutes, so as to minimise disruption of the surrounding water structure. Because of the strong π-π interactions between adjoining dye molecules and the screening effect exerted by the electrolyte Na^+ counter-ions, ionisation of the dye molecules is supressed, so that the ensuing dye aggregates possess lower aqueous solubility than their non-aggregated dye counterparts.

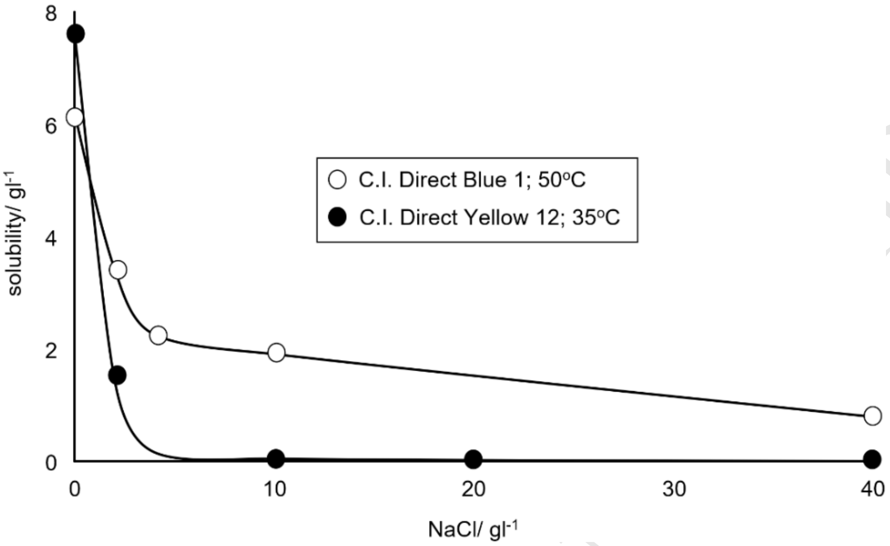


Figure 1 effect of NaCl on the solubility of purified C.I. Direct Blue 1 and C.I. Direct Yellow; plotted using data from (9)

In this context, the remarkable ability of NaCl to impart major reductions in the aqueous solubility of direct dyes is demonstrated by the data shown in Figure 1 (9). As mentioned, since the immersion application of direct dyes to cellulosic fibres is typically carried out in the presence of between 5 gl^{-1} and 20 gl^{-1} added NaCl or Na_2SO_4, it is apparent from Figure 1, that the addition of such amounts of added electrolyte to direct dye dyebaths will likely impart sizeable reductions in dye solubility. Thus, when inorganic electrolyte is added to a direct dye dyebath, the solubility of the dye is markedly reduced so that the inherent predisposition of the dye to remain in the aqueous dyebath in the absence of added electrolyte will be significantly diminished. Consequently, the dyes display much greater substantivity towards the cellulosic fibre and, therefore, in the presence of added inorganic electrolyte, dye uptake is promoted.

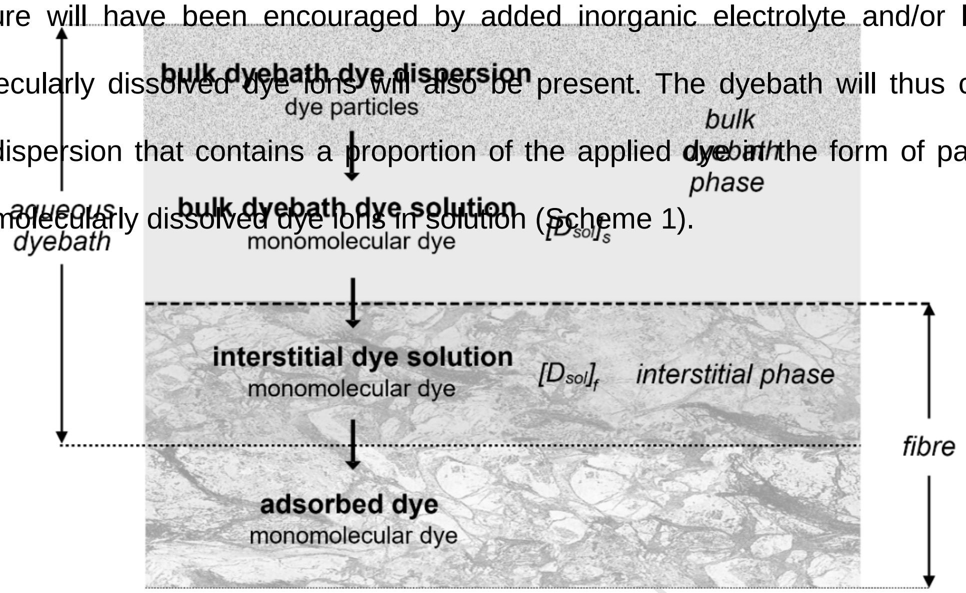
1.2.1 interstitial water

The impact of these dyebath events on the immersion dyeing system can be explained according to the notion that dyeing takes place from within interstitial dye solution located in the fibrous substrate. Briefly, the concept of interstitial water in dyeing processes (3, 4), which has been used to develop both novel dyeing (10) and wash-off (11-14) processes for various dye-fibre systems as well as an innovative commercial clothes washing system (15-18), is based on the premise that of the water used in exhaust dyeing, only a very small proportion that resides within the interstices of the fibrous substrate is required to saturate the textile substrate and impart the crucially important actions of fibre wetting and fibre swelling. In accordance with the concept of free and bound sorbed water molecules and electric double-layer theory, it is considered (3) that interstitial water will differ to that which resides within the surrounding bulk dyebath because of the influences of the charged textile fibre surface and the reduced mobility of the bound water molecules on the distribution of sorbed ions/molecules. It is assumed that because this interstitial water within the wetted, swollen fibre comprises dyebath solution and is in intimate contact with and a fundamental component of, the swollen fibre, the transfer of dye molecules from the dyebath to the fibre takes place from within this interstitial water. The remaining vast majority of the water that is used in immersion dyeing is present within the bulk dyebath that surrounds the water-swollen fibre and provides functions such as heating, agitation, dye dissolution, mechanical agitation, etc. (3).

The volume of interstitial water present within cotton and other cellulosic substrates is assumed (3, 4) to correspond to the moisture regain of the substrate at 100% relative humidity (*RH)*, which is commonly reported as 0.22 l kg^{-1} (19). The crucial role of interstitial water in immersion dyeing is the subject of a subsequent part of this paper.

In terms of the dyeing of cellulosic fibres with direct dyes, it is possible to explain the promotional effect of both reduced liquor ratio and added inorganic electrolyte on dye uptake in terms of the interstitial dyeing mechanism; the process depicted in Scheme 1 can be considered to apply (3, 4).

At the start of dyeing, the aqueous dyebath, which comprises both the bulk dyebath phase and the interstitial phase, will contain a sizeable number of dye particles (ie aggregates of dye molecules) because the inherent predisposition of the direct dye molecules to self-associate in solution at low temperature will have been encouraged by added inorganic electrolyte and/or low liquor ratio; monomolecularly dissolved dye ions will also be present. The dyebath will thus comprise a bulk dyebath dispersion that contains a proportion of the applied dye in the form of particles, together with monmolecularly dissolved dye ions in solution (Scheme 1).



Scheme 1 representation of direct dyeing mechanism (3, 4)

As dyebath temperature increases, so dye aggregation will decrease and, therefore, the proportion of dissolved dye molecules will increase as the quantity of dye aggregates in the dyebath falls; however, dye particles are likely still present in the dyebath phase. Dissolved dye molecules within the interstitial solution interact with the substrate (eg by a Freundlich-type or Langmuir-type process) and become adsorbed. Dye molecules which are present in the bulk dyebath solution then transfer to the interstitial dye solution from which further dye molecules can be adsorbed onto the substrate. The bulk dyebath solution is then replenished by the transfer of dye molecules which are released from the dye particles in the bulk dyebath dispersion. Thus, dissolved dye ions are able to transfer from the bulk dyebath solution to the interstitial dye solution in the fibre from which further dye adsorption can occur. This process of dye dissolution from the bulk dyebath dispersion to the bulk dyebath solution, dye molecule transfer from the bulk dyebath solution to the interstitial dye solution and subsequent 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.

According to the notion that direct dye adsorption takes place from within interstitial dye solution, then in order to achieve complete dye exhaustion in immersion dyeing, the intrinsic inclination of dye molecules to diffuse from the dyebath phase to the fibre phase under the influence of a dye concentration gradient between the two phases, must be augmented by dye-fibre substantivity (3). In commercial immersion dyeing processes, as the level of dye-fibre substantivity is routinely manipulated (eg using pH adjustment, dyeing auxiliaries, temperature, etc.) so as to achieve uniform dyeings of the desired depth of shade in the required period of time, it was reasoned (3) that such manipulations principally regulate the solubility of the dye in the aqueous dyebath. As such, the main factor which determines dye-fibre substantivity and, therefore, the tendency of the dye to favour either the fibre or dyebath phase, is the solubility of the dye in the dyebath (3).

The link between dye solubility and dye-fibre substantivity depicted in Scheme 1 can be described by Eq 1 (3) where *[D]* is the total amount of dye within the immersion dyeing system, which comprises dye that is present in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$ as well as that present in the bulk dyebath dye solution in the dyebath phase, $[D_{sol}]_s$, and *S* is the substantivity coefficient of the dye.

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

In terms of the application of direct dyes to cellulosic fibres, Eq 1 revealed that the partition of a direct dye between the fibre and dyebath phases depends on the concentration of dye within the bulk dyebath solution phase, $[D_{sol}]_s$. Adding inorganic electrolyte to an aqueous direct dyebath (3) is considered to be a dilution effect insofar as, either NaCl or Na_2SO_4 induce dye aggregation, which reduces the solubility of the dye, as a result of which, the amount of dye in solution within the dyebath phase, $[D_{sol}]_s$, is reduced. Since Eq 1 shows that the spontaneous movement of dye molecules from the aqueous phase (dyebath) to the solid phase (fibre) (ie the driving force for dyeing), is the concentration gradient, $[D_{sol}]_f/[D_{sol}]_s$, between the amount of dye in the dye solution within the bulk dyebath, $[D_{sol}]_s$, and the amount of dye in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$, it follows that in the presence of added inorganic electrolyte, 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 increase, so that a higher driving force for dyeing will be established. Thus, according to Eq 1, the partition of the dye between the fibre and solution phases, $[D_{sol}]_f/[D_{sol}]_s$ (ie S) will increase in the presence of added NaCl or Na_2SO_4 because the amount of dye in the dye solution within the bulk dyebath, $[D_{sol}]_s$, has been lowered and, therefore, the amount of dye in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$, has increased accordingly.

Since Eq 1 describes the transfer of dye from the bulk dyebath dye solution, $[D_{sol}]_s$, to the interstitial dye solution, $[D_{sol}]_f$ then both $[D_{sol}]_f$ and $[D_{sol}]_s$ and, of course, $[D]$, can be expressed as mass per unit volume (eg g l^{-1}); because of the term ($[D] - [D_{sol}]_s/[D_{sol}]_s$), substantivity coefficient S also has dimensions of mass per unit volume (eg gl^{-1}).

As such, Eq 1 shows that the inherently low substantivity displayed by direct dyes towards cellulosic fibres in the absence of added electrolyte arises because of the dye's preference for the dyebath phase, which stems from the dye's high solubility (ie $[D_{sol}]_s$) (3, 4). Thus, Eq 1 is able to explain why the addition of NaCl or Na_2SO_4 to a direct dyebath increases dye-fibre substantivity, as expressed by the substantivity coefficient, S, and, as a consequence, the partition of the dye shifts away from the aqueous phase towards the fibre phase (ie $[D_{sol}]_f$) > $[D_{sol}]_s$).

According to this theoretical approach (3, 4), added electrolyte promotes direct dye uptake because of the combined effects of induced dye aggregation and consequential reduced dye solubility on the dye concentration gradient between the fibre and dyebath phases. Thus, it is the effects which added electrolyte has upon the concentration of dye in the dyebath solution phase (ie the dyebath) that determines the amount of dye in the fibre solution phase (ie the fibre).

1.3 the role of liquor ratio in the dyeing of cellulosic fibres using direct dyes

The aqueous solubility of direct dyes conferred by the presence of one or more sulfonate groups is mostly responsible for the renowned simplicity and inherent robustness of the immersion direct dyeing process (3). However, the typically very good aqueous solubility of direct dyes is of major significance in terms of the mechanism of their adsorption onto cellulosic fibres and the role of added electrolyte in dye uptake. The influence of dye solubility on dyeing is demonstrated by the fact that the liquor ratio used for dyeing has a pronounced effect on both the rate and extent of dye uptake. Furthermore, liquor ratio, and thereby, the solubility of the dye in the aqueous dyebath, has a direct impact on the effectiveness with which added electrolyte promotes dye uptake. The liquor ratio utilised in direct dyeing influences the substantivity of the dye towards the fibre, since the amount of water in the dyebath available for dye dissolution, and thus the amount of dye available for adsorption on the fibre, is determined by liquor ratio. In addition, as the dye concentration in the dyebath is determined by liquor ratio then so the intensity of the electrolyte-dye interactions that result in promoted dye uptake are influenced by liquor ratio.

In the commercial application of direct dyes to cellulosic fibres using immersion processes, the level of substantivity displayed by the dye towards the cellulosic substrate is manipulated, by using a given amount of added inorganic electrolyte in combination with a particular liquor ratio (at a given dyeing temperature), so that the relative contributions towards dye-fibre substantivity imparted by added electrolyte and liquor ratio are controlled. Thus, if the liquor ratio used for dyeing is changed, the amount of added electrolyte utilised must also be changed accordingly, so that the level of dye-fibre substantivity secured is consistent with that required to achieve uniform dyeings of the desired depth of shade (within a preferred duration).

Despite much attention over many decades, confusion has surrounded the precise mechanism by which liquor ratio influences the immersion application of direct dyes on cellulosic fibres (as well as that of all classes of dye on various types of substrate). Furthermore, uncertainty has attended the combined effects which liquor ratio and added inorganic electrolyte exert upon direct dye uptake.

In this context, it was proposed (4) that the theoretical model of direct dyeing which explained the promotional effect of added inorganic electrolyte on direct dye uptake (section 1.2) could also be used to describe the promotion of direct dye uptake on cellulosic fibres imparted by a reduction in the liquor ratio used for dyeing. Eq 2 (a derivative of Eq 1) was derived, where *L* is the fractional liquor ratio (where *L* = fibre mass/dyebath volume (3)), according to which, because of the term ($[D_{sol}]_s/L$), liquor ratio, via *L*, impacts directly on the amount of dye in solution in the bulk dyebath phase, $[D_{sol}]_s$, rather than on the amount of dye in the interstitial solution in the fibre, $[D_{sol}]_f$, insofar as, values of $[D_{sol}]_s$ will decrease with decreasing liquor ratio and, therefore, values of $[D_{sol}]_f$ will increase accordingly.

$$S = \frac{[D_{sol}]_f}{\frac{[D_{sol}]_s}{L}} = \left(\frac{[D] - \frac{[D_{sol}]_s}{L}}{\frac{[D_{sol}]_s}{L}} \right) \qquad 2$$

As the proclivity of direct dyes to self-associate in aqueous solution via coplanar association is encouraged in solutions of high dye concentration, such a situation can be expected to arise in dyebaths of low liquor ratio. When the liquor ratio used for dyeing is lowered, the amount of water in the dyebath in which the direct dye molecules can dissolve is lowered and, therefore, the initial dye concentration in the dyebath will increase accordingly. Because of the marked tendency of direct dyes to aggregate in aqueous solution, which accrues from the characteristic planar structure of the dye anions and the likelihood of π-π interactions between aromatic regions within adjoining dye molecules, the combined effects of a reduced amount of water available for dye dissolution (ie reduced dyebath volume) and greater initial dye concentration in the dyebath, will serve to encourage dye aggregation. The aqueous solubility of the ensuing aggregates will be lower than that of their monomolecular direct dye antecedent because hydrophobic interaction will promote strong dye-dye interactions and supress ionisation of the dye molecules.

Thus, lowering the liquor ratio used for dyeing will reduce the solubility of the dye, which therefore reduces the amount of dye in the dye solution in the bulk dyebath phase, $[D_{sol}]_{s}$, and, therefore, from Eq 2, the value of $[D_{sol}]_{f}/[D_{sol}]_{s}/L$ will increase, so the partition of the dye will favour the fibre and dyeing is promoted. Thus, reducing the liquor ratio used for direct dyeing is analogous to that of adding inorganic electrolyte to the dyebath insofar as both actions lower the concentration of dye in the dye solution within the dyebath phase.

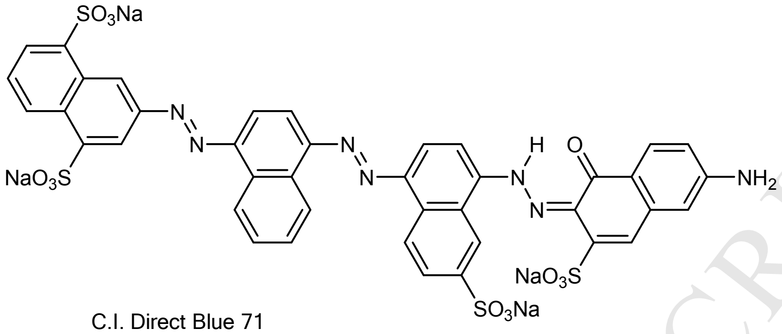
Adding inorganic electrolyte to a direct dye dyebath (3) and/or reducing the liquor ratio used for dyeing (4) therefore achieve the same outcome, namely promotion of dye uptake. Indeed, according to Eq 1 and Eq 2, the increased uptake of direct dyes that accompanies both the addition of inorganic electrolyte to a direct dyebath and a reduction in the liquor ratio employed for dyeing can, in essence, be considered as a process of controlled precipitation of the dye within the fibre. Thus, the use of very low liquor ratios should, theoretically, enable dyeing to be achieved in the absence of added inorganic electrolyte.

2 Experimental

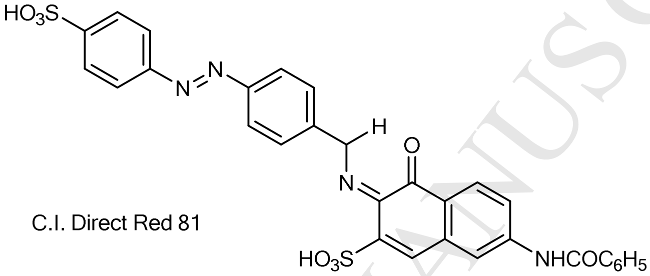
2.1 Materials

Scoured, bleached and mercerised woven cotton fabric (180 gm^{-2}) was obtained from Whaleys (Bradford, UK). Commercial samples of three direct dyes, namely C.I. Direct Blue 71, C.I. Direct Red 81 and C.I. Direct Yellow 50 were obtained from Sigma-Aldrich. All other chemicals were of general purpose grade.

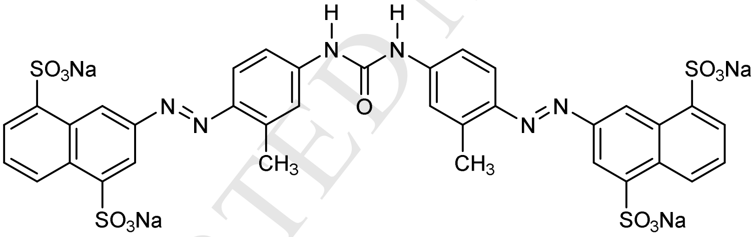
The three dyes used were chosen arbitrarily as being representative of modern commercial direct dyes. A 2% omf depth of shade was used for each of the three dyes as this provided typical pale/medium depth dyeings.



C.I. Direct Blue 71



C.I. Direct Red 81



C.I. Direct Yellow 50

2.2 Dyeing

2% omf dyeings were carried out using various liquor ratios in both the presence and absence of 20 gl^{-1} NaCl. The amount of added electrolyte in dyeing was adjusted to ensure that a concentration of 20 gl^{-1} was employed, regardless of liquor ratio employed. Two dyeing methods were used; in each case, at the end of dyeing, the dyed sample was removed from the dyebath, squeezed to remove surplus dye liquor and rinsed under cold running tap water for 5 minutes and then allowed to dry in the open air.

2.2.1 dyeing tubes/dyeing machine

Dyeings were carried out according to the dye maker's recommendations, following the procedure shown in Figure 2, employing liquor ratios of 1:50, 1:20, 1:10, 1:6 and 1:3, in sealed, 300 cm^3 capacity, stainless steel dyepots housed in a *Roaches Pyrotec S* dyeing machine.

2.2.2 PP bags/tumble dryer

Dyeings were undertaken, employing liquor ratios of 1:2, 1:1.5 and 1:1, in sealed, 1000 cm^3 capacity, polypropylene plastic bags housed in a *Miele PT8257* tumble dryer, following the procedure shown in Figure 3.

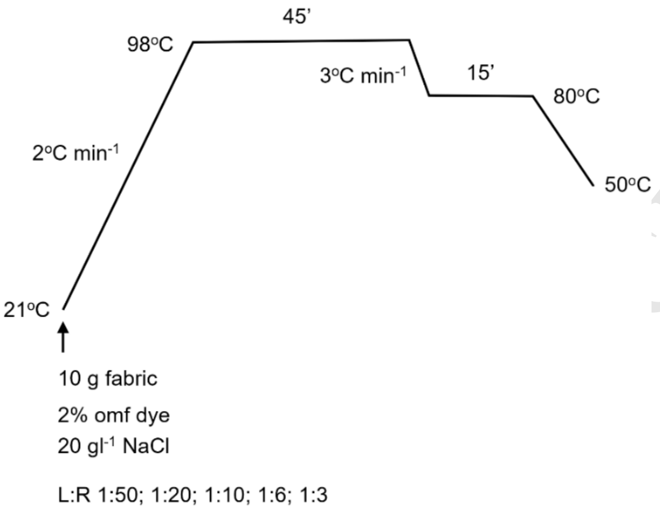


Figure 2 dyeing tube/dyeing machine dyeing method

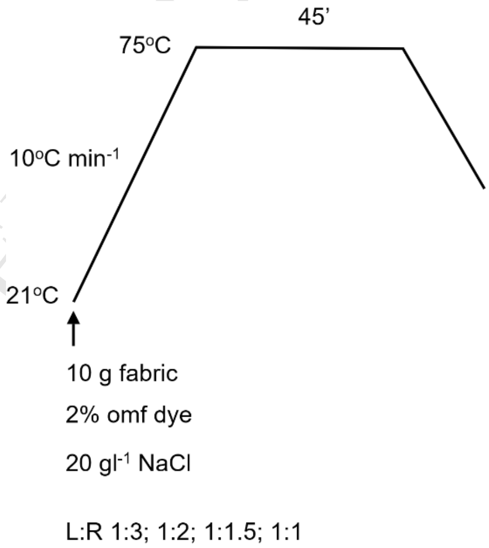


Figure 3 PP bag/tumble dryer dyeing method

2.3 Colour measurement

The CIE colorimetric co-ordinates and colour strength (f_k) values of the dyeings were calculated from the mean K/S values for each dyeing as measured using a *Datacolour Spectroflash 60* reflectance spectrophotometer from 400 nm to 700 nm using D_{65} illuminant, 10° standard observer with UV component included and specular component excluded. Samples were folded so as to realise two thicknesses and the average of four measurements was taken for each sample.

2.4 Measurement of dye exhaustion

The extent of dye exhaustion was determined spectrophotometrically. The absorbance at λ_{max} of a suitably diluted (distilled water) sample of dye liquor taken both before dyeing and after dyeing was determined using a 1 cm path quartz cell housed in a Perkin-Elmer *Lambda 9* UV/Visible/NIR spectrophotometer in the region 400–700 nm. The percentage dyebath exhaustion, *%E*, was calculated using Eq 3 where A_0 and A_1 represent the absorbance of the dye solution before and after dyeing, respectively.

$$\%E = 100 \times \left(1 - \frac{A_1}{A_0}\right) \qquad 3$$

3 Results and Discussion

As mentioned, this part of the paper concerns the exhaust application of direct dyes to cotton and the role of the most fundamentally important dyeing auxiliary utilised in this dyeing system, namely added inorganic electrolyte, in the form of sodium chloride. Results are presented for dyeings on cotton carried out using commercial direct dyes, at various liquor ratios in both the absence and presence of 20 gl^{-1} added NaCl. The results of these practical results are interpreted in terms of the previously developed theoretical models (3, 4) that seek to describe the manner by which inorganic electrolytes such as NaCl and Na_2SO_4 as well as reduced liquor ratio promote the uptake of direct dyes on cellulosic fibres during immersion dyeing.

3.1 the need to use two dyeing methods

As described in section 2.2, dyeings were carried out using two methods, namely one that employed 300 cm^3 capacity, stainless steel dyepots housed in a *Roaches Pyrotec S* dyeing machine, following the procedure recounted in 2.2.1 as well one that employed sealed, 1000 cm^3 capacity, polypropylene plastic bags housed in a *Miele PT8257* tumble dryer, as described in 2.2.2. The reasons as to why the two methods were employed are now discussed.

An often cited concern associated with the use of low liquor ratios in exhaust dyeing is the control of dye migration and, thus, the production of level dyeings (1). Indeed, in this work, it was found that whilst both the shape of the particular 300 cm^3 capacity, stainless steel dyepots and the mechanism of agitation employed in the *Roaches Pyrotec S* dyeing machine were very well suited to dyeing at liquor ratios throughout the range 1:50 to 1:3, using the cotton fabric and dyes employed in this work, insofar as consistently level dyeings were secured; however, inconsistently level dyeings were achieved when liquor ratios <1:3 were employed. Consequently, an alternative dyeing vessel/agitation method was developed that enabled level dyeings to be achieved over the range of liquor ratios 1:3 to 1:1, namely, sealed, 1000 cm^3 capacity, polypropylene plastic bags housed in a *Miele PT8257* tumble dryer. However, as the uniformity of the dyeings obtained using the PP bag/tumble dryer method employing a 1:1 liquor ratio was not always perfect in the case of dyeings carried out in the presence of 20 gl^{-1} added NaCl, the results obtained for 1:1 liquor ratio dyeings undertaken in the presence of added inorganic electrolyte are not included in this part of the paper.

There are several likely causes of the unlevelness observed at such low liquor ratios, such as the solubility of the dye in the dyebath having been reduced because of increased dye aggregation or an increase in the rate of dye strike resulting from a corresponding increase in the dye concentration in the dyebath. Such unlevelness usually implies that the level of dye-fibre substantivity within the dyebath was too high. Both the origins of such high dye-fibre substantivity and possible ways of avoiding it so that level dyeings can be achieved at ultra-low liquor ratios (ie 1:1.5 and 1:1) are discussed below.

The high level of consistency of the dyeings carried out at liquor ratios of ≤1:3 using the PP bag/tumble dryer method (with the exception of those secured using a 1:1 liquor ratio in the presence of added NaCl) can be attributed to the larger capacity (1000 cm^3) dyeing container and the random, tumbling action of the commercial tumble dryer having providing greater fabric:dye liquor interchange.

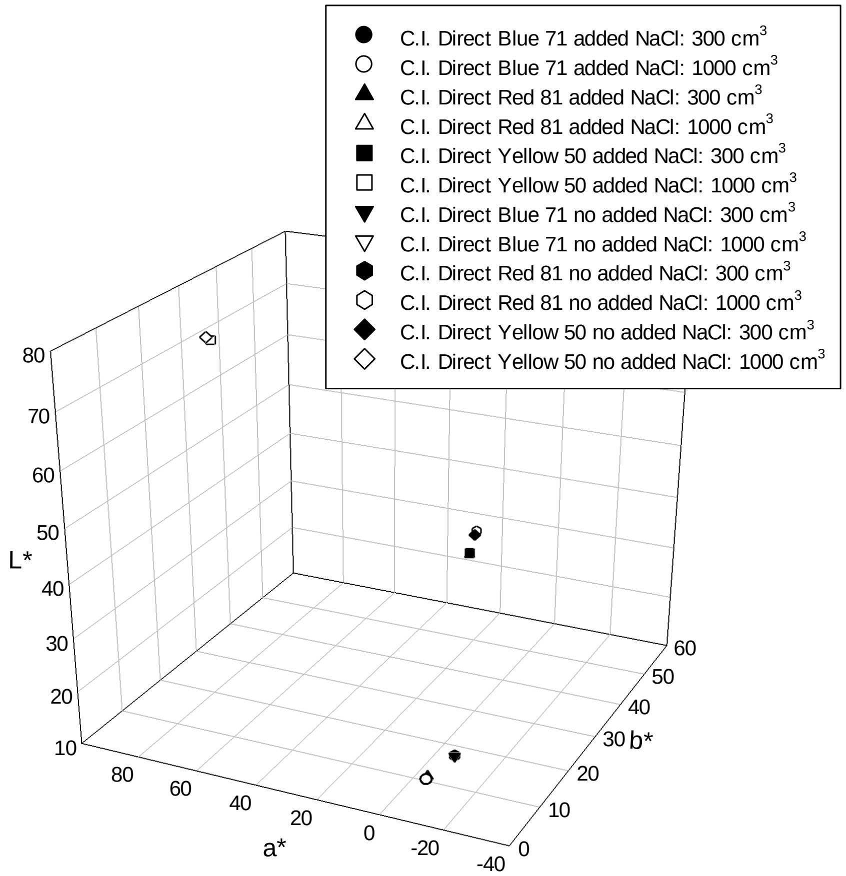


Figure 4 comparison of dyeings achieved using dyeing tube/ dyeing machine and PP bag/tumble dryer dyeing methods; 1:3 liquor ratio; absence and presence of 20 gl^{-1} NaCl

To determine the compatibility of the two dyeing methods, an analysis was undertaken of dyeings, carried out in both the absence and presence of 20 gl^{-1} added NaCl, using a 1:3 liquor ratio employing both dyeing tube/ dyeing machine and PP bag/tumble dryer methods, as consistently level dyeings were achieved using this particular liquor ratio for both dyeing methods. It was found that there were only small colorimetric differences between the dyeings which had been carried out using the two dyeing methods.

This is shown by the L*, a* and b* data displayed in Figure 4 and the findings that the ΔE_{CIELAB} values calculated between corresponding dyeings were <<1.0. Furthermore, the closeness of the colour strength data secured for the respective dyeings obtained using the two types of dyeing vessel/agitation system confirmed that the dyeing methods were compatible in terms of the quality (depth of shade, hue and chroma) of the dyeings produced.

Thus, in this work, results are presented for dyeings that were carried out over the range of liquor ratios 1:50, 1:20, 1:10, 1:6 and 1:3 using the dyeing tubes/dyeing machine dyeing method described in 2.2.1 and at liquor ratios of 1:2, 1:1.5 and 1:1 (the latter only in the absence of added electrolyte) using the PP bags/tumble dryer dyeing method described in 2.2.2.

3.2 colour strength

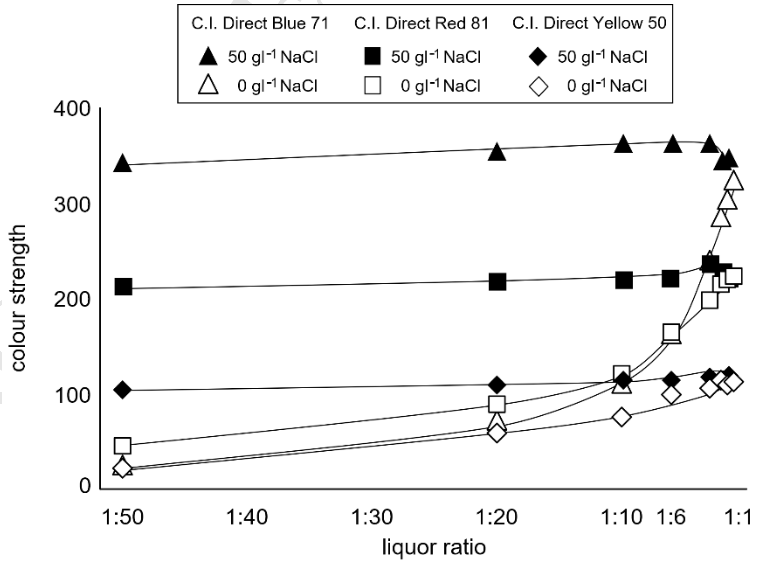


Figure 5 Effect of liquor ratio on colour strength; absence and presence of 20 gl^{-1} NaCl

Figure 5 shows the effect of varying the liquor ratio used in dyeing from 1:50 to 1:1 on the colour strength (f_k values) obtained for 2% omf dyeings on woven cotton fabric, in both the absence and presence of 20 gl^{-1} added NaCl.

The corresponding colorimetric data obtained for the dyeings are displayed in Table 1, which reveal that reducing the liquor ratio from 1:50 to 1:1 did not result in any changes in the colour of the dyeings, as expected; also, the colour of the dyeings was the same regardless of whether dyeing had been undertaken in the presence or absence of added sodium chloride.

Table 1 Colorimetric parameters for 2% omf dyeings; absence and presence of 20 gl^{-1} NaCl

liquor ratio	C.I. Direct	NaCl/gl^{-1}	L*	a*	b*	C*	h°	λ_{max}
1:50	Blue 71	20	16.2	3.6	-11.4	12.0	287.4	580
		0	52.6	-1.8	-25.3	25.4	265.9	600
	Red 81	20	32.6	48.6	19.0	52.2	21.3	520
		0	51.4	52.9	10.5	53.9	11.3	
	Yellow 50	20	74.4	24.8	86.9	90.4	74.0	420
		0	83.9	6.5	64.6	64.9	84.1	
1:20	Blue 71	20	15.7	3.6	-11.2	11.8	288.0	580
		0	31.6	46.6	17.6	49.8	20.7	600
	Red 81	20	31.6	46.6	17.6	49.8	20.7	520
		0	72.8	25.7	85.4	89.2	73.2	
	Yellow 50	20	72.8	25.7	85.4	89.2	73.2	420
		0	78.8	17.1	80.6	82.4	78.0	
1:10	Blue 71	20	15.5	3.8	-11.2	11.8	289.0	580
		0	30.6	3.8	-26.9	27.1	278.1	600

	Red 81	20	31.8	47.3	18.3	50.7	21.1	520
		0	39.7	52.3	17.6	55.2	18.6	
	Yellow 50	20	72.0	27.5	85.1	89.5	72.1	420
		0	76.7	19.9	83.3	85.6	76.5	
1:6	Blue 71	20	15.5	3.8	-10.6	11.3	289.8	580
		0	25.2	4.8	-23.7	24.2	281.4	600
	Red 81	20	31.6	47.0	18.2	50.5	21.1	520
		0	35.2	48.6	17.3	51.6	19.6	
	Yellow 50	20	72.5	27.3	86.1	90.3	72.3	420
		0	74.8	24.5	86.3	89.7	74.2	
1:3	Blue 71	20	15.5	3.7	-10.5	11.2	289.6	580
		0	20.1	4.7	-18.3	18.9	284.3	600
	Red 81	20	30.4	45.1	17.4	48.3	21.0	520
		0	33.3	48.5	18.3	51.8	20.7	
	Yellow 50	20	72.3	27.4	86.1	90.4	72.3	420
		0	73.5	25.8	85.5	89.3	73.2	
1:2	Blue 71	20	16.0	4.0	-10.9	11.6	290.2	580
		0	18.0	4.7	-15.2	15.8	287.3	600
	Red 81	20	30.6	44.7	17.2	47.9	21.0	520
		0	32.1	47.3	18.2	50.7	21.0	
	Yellow 50	20	72.2	27.5	85.6	89.9	72.1	420
		0	72.4	27.2	85.7	89.9	72.38	
1:1.5	Blue 71	20	15.9	3.8	-11.3	11.9	288.9	580

		0	17.3	4.4	-13.6	14.3	288.1	600
	Red 81	20	31.2	45.6	17.5	48.8	21.0	520
		0	31.7	46.8	18.0	50.2	21.0	
	Yellow 50	20	71.9	28.1	86.1	90.6	71.9	420
		0	72.7	26.9	85.1	89.2	72.4	
1:1	Blue 71	20	unlevel					
		0	16.6	4.1	-12.3	13.0	288.7	600
	Red 81	20	unlevel					
		0	31.0	45.2	17.6	48.4	20.9	520
	Yellow 50	20	unlevel					
		0	72.0	27.0	84.7	88.8	72.3	420

No colour yield or colorimetric data is presented in Table 1 or Figure 5 for dyeings that were carried out at liquor ratios of 1:1 in the presence of added NaCl, owing to the dyeings being unlevel. This failure to achieve satisfactorily level dyeings can be partly attributed to the direct dyes having precipitated in the presence of added electrolyte, due to aggregation in the dyebath, even at the high dyeing temperature used (98^{o}C). In the latter context, whilst it is often considered that high dyeing temperatures tend to disfavour direct dye aggregation, as the dyes exhibit low aggregation under immersion dyeing conditions (20), aggregation has been observed at 90^{o}C in the presence of electrolyte (21).

3.3 dye exhaustion

The data presented in Figure 6 reveals that a marked difference was observed between the effect of liquor ratio on the extent of dye exhaustion achieved in the absence and presence of added electrolyte. Although reducing the liquor ratio used for dyeing imparted only a modest increase in dye uptake in the case of dyeings carried out in the presence of 20 gl^{-1} added electrolyte, for dyeings undertaken in the absence of added electrolyte, the effect of decreasing liquor ratio on dye uptake was significant, for each of the three dyes used.

It is also apparent from Figure 6 that in the case of dyeings which had been carried out in the presence of 20 gl^{-1} added NaCl, dye exhaustion increased with decreasing liquor ratio over the range 1:50 to 1:3 and thereafter remained reasonably constant with further reduction in liquor ratio to 1:1.5. Hence, the findings (Figure 5) that colour yield increased with decreasing liquor ratio over the range 1:50 to 1:3 and then remained little changed with further reduction in liquor ratio to 1:1.5, correlates with the corresponding dye exhaustion values obtained (Figure 6). Indeed, Figure 6 shows that in the case of dyeings carried out in the absence of added NaCl, the observed increase in colour strength of the dyeings that accompanied a reduction in liquor ratio over the range 1:50 to 1:1 (Figure 5) can be attributed to a corresponding increase in dye exhaustion.

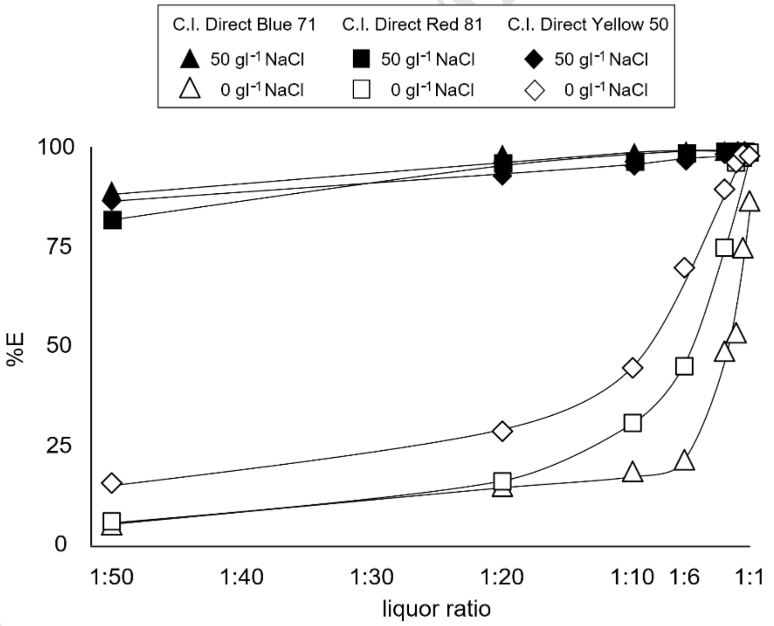


Figure 6 effect of liquor ratio on dye exhaustion; absence and presence of 20 gl^{-1} NaCl

As discussed previously (3), liquor ratio controls the amount of water available in a dyebath for dye dissolution/dye dispersion to occur and, therefore, liquor ratio governs both the rate and extent of dye transfer from the aqueous dyebath to the fibre, since it determines the magnitude of the concentration gradient that exists between the amount of dye in solution in the bulk dyebath phase, $[D_{sol}]_s$, and the amount of dye in the interstitial dye solution in the fibre phase, $[D_{sol}]_f$, which, in turn, determines the distribution of dye between the aqueous and fibre phases, as described by Eq 2.

Thus, when dyeing was carried out in the absence of added NaCl (Figure 6), the promotion of dye uptake imparted by lowering the liquor ratio over the complete range of liquor ratios used (ie 1:50 to 1:1), can be explained in terms of the combined effects which increased dye aggregation and reduced dye solubility had upon the concentration gradient that exists between the amounts of dye in the dyebath and fibre phases (3). Lowering the liquor ratio reduced the amount of water in the dyebath which therefore increased the concentration of dye in the dye solution within the bulk dyebath, $[D_{sol}]_s$. This encouraged dye aggregation which further lowered $[D_{sol}]_s$, with the result that both the dye concentration gradient, $[D_{sol}]_f/[D_{sol}]_s$, and the driving force for dyeing increase. Hence, the distribution of dye between the aqueous and fibre phases shifts towards the fibre phase and, therefore, dye uptake increases with decreasing liquor ratio, as was observed (Figure 6).

As discussed, this particular explanation of the manner by which reduced liquor ratio promotes the uptake of direct dyes on cellulosic fibres was shown to essentially parallel that which describes the promotion of direct dye uptake imparted by added inorganic electrolyte (3). Thus, reducing the liquor ratio used in dyeing and adding electrolyte to the dyebath impart the same promotional effect on direct dye uptake, in that, both actions increase dye aggregation and lower the solubility of the dye in the dyebath (3). Therefore, the degree to which direct dye uptake is enhanced will be greatest when the promotional effects of added NaCl and reduced liquor ratio are maximal, which will occur when low liquor ratio dyeings are undertaken in the presence of added electrolyte and will be lowest when the promotional effects of reduced liquor ratio and added electrolyte are minimal, as will arise when high liquor ratio dyeings are carried out in the absence of added electrolyte.

Accordingly, when dyeing had been carried out in the presence of added electrolyte, the extent of dye exhaustion achieved at a given liquor ratio should have been greater than that observed in the absence of added NaCl, as was observed (Figure 6). Furthermore, since both adding electrolyte and reducing liquor ratio promote dye uptake, then when dyeing was carried out in the presence of 20 gl^{-1} added NaCl, the promotional effect imparted by the added electrolyte should be lower at higher liquor ratios than at lower liquor ratios, as was also observed (Figure 6). In addition, the extent of dye exhaustion should increase with decreasing liquor ratio, irrespective of whether or not dyeing had been carried out in the presence of added electrolyte, as was observed (Figure 6).

3.4 promotional effect of added electrolyte and reduced liquor ratio on dye-fibre substantivity

As mentioned, in commercial immersion dyeing processes for applying direct dyes to cotton (and other cellulosic fibres), the level of dye-fibre substantivity within the dye/electrolyte/fibre system is manipulated by the dyer so that uniform dyeings of the desired colour strength are obtained within the desired time frame. This is achieved by employing a given amount of added electrolyte in conjunction with a particular liquor ratio (at a given temperature) so that the relative contributions that added electrolyte and liquor ratio make towards dye-fibre substantivity are regulated. Thus, dyeing at high liquor ratios in the absence of added electrolyte will result in the dye displaying low substantivity towards the cellulosic fibre, whereas dyeing at low liquor ratios in conjunction with the use of large amounts of added electrolyte will result in high dye-fibre substantivity. From this it follows that high liquor ratio dyeing generally results in low dye uptake whereas dyeing at low liquor ratios generally provides high dye uptake.

In this context, the results displayed in Table 1 and Figures 5 and 6 describe the enhancement of colour strength and dye exhaustion imparted by the addition of 20 gl^{-1} NaCl to dyeings. This data also describes the promotion of dye uptake and colour strength that was imparted by reducing the liquor ratio employed for dyeing. As such, the results cover a wide span of dye-fibre substantivity that ranges from very low in the case of high liquor ratio dyeings in the absence of added NaCl to very high in the case of dyeings carried out at low liquor ratios in the presence of 20 gl^{-1} NaCl. An attempt was therefore made to distinguish the impacts on dye uptake of added electrolyte from those of reduced liquor ratio.

$$\text{\% promotional effect} = \frac{\text{\%E in presence of added NaCl -\%E in absence of added NaCl}}{\text{\%E in presence of added NaCl}} \times 100 \qquad 4$$

The effect of added electrolyte on dye uptake and its variation as a function of liquor ratio can be quantified using the *promotional effect*, calculated using Eq 4, which expresses the proportional contribution that added NaCl made to the extent of dye exhaustion achieved at a particular liquor ratio as a percentage.

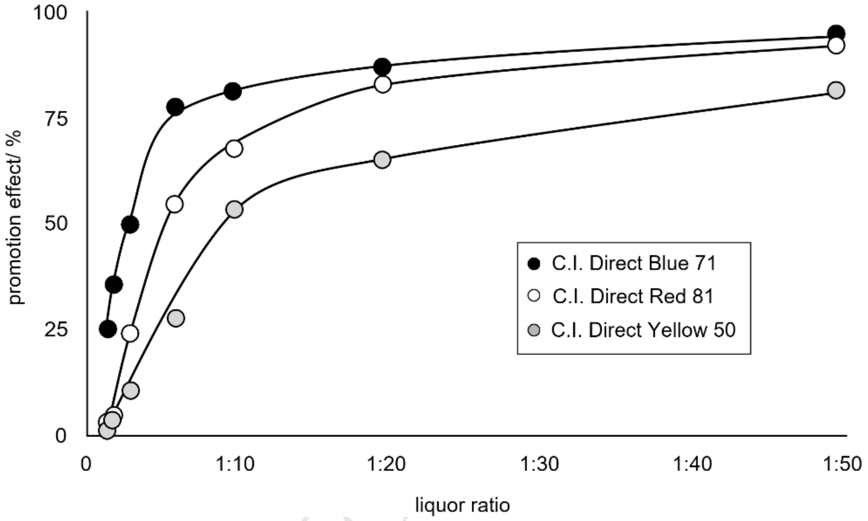


Figure 7 promotional effect of added electrolyte on colour strength

Figure 7 shows the magnitude of the promotion effect imparted by adding 20 gl^{-1} NaCl to the dyebath as a function of liquor ratio, for each of the three dyes used. The finding that the extent of this promotion of dye exhaustion decreased with decreasing liquor ratio reveals that the ability of the added electrolyte to enhance dye exhaustion diminished with decreasing liquor ratio. In turn, this means that added electrolyte was more effective in promoting dye uptake at long liquor ratios (ie 1:50) than at short liquor ratios (ie 1:1.5), even though a constant concentration (ie 20 gl^{-1}) of added NaCl had been employed at each liquor ratio examined.

If the proposal (3) that the manner by which reduced liquor ratio promotes uptake of the three direct dyes is the same as that by which dye uptake is promoted by adding inorganic electrolyte, then reducing the liquor ratio used in dyeing and adding electrolyte to the dyebath will have the same effect on direct dye uptake, namely, they will lower the effective concentration of dye in the dyebath owing to the effects of dye aggregation and reduced dye solubility in the dyebath. Accordingly, the extent to which dye uptake is enhanced by added NaCl will be greatest when the promotional impact of reduced liquor ratio is lowest, as is the case of high liquor ratio dyeings, and will be lowest when the promotional impact of reduced liquor ratio is greatest, as is the case when low liquor ratio dyeings are undertaken. Thus, the promotional effect of the added 20gl^{-1} NaCl on direct dye uptake should decrease with decreasing liquor ratio, as was observed (Figure 7).

3.4.1 interpretation of results using theoretical model

Eq 5 describes the partition of a dye between the fibre phase and the solution (dyebath) phase where $[D]_f$ 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 and the equilibrium partition coefficient, K, describes the distribution of the dye between the dyebath, s and fibre, f, phases.

$$K = \frac{[D]_f}{[D]_s} \qquad 5$$

As discussed (3, 4), equations based upon Eq 5 are often used in studies that seek to determine the mechanism by which dye adsorption proceeds when equilibrium dye uptake has been achieved.

Based on the assumption that dye solubility is the key determinant of dye-fibre substantivity and, also, that the solubility of the dye in the dyebath phase determines the relative partition of the dye between the fibre and dyebath phases (ie the extent of dye uptake), it is possible to interpret the effect of liquor ratio on the distribution of the dye between the fibre and dyebath phases that is achieved at the end of an immersion dyeing process using the partition described by Eq 5, via Eq 6 (4), even though equilibrium dye uptake is not achieved.

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

Eq 6 describes the relationship between the partition of the dye between the fibre, $[D]_f$, and solution, $[D]_s$, phases, expressed in terms of the substantivity coefficient, S, and the fractional liquor ratio, L, (4). The ratio $[D]_f/[D]_s/L$ describes the relative partition of the dye between the fibre and dyebath phases and, therefore, represents the substantivity displayed by the direct dye towards the substrate, which is expressed by the substantivity coefficient of the direct dye at the end of the immersion dyeing process, S: the higher the value of this ratio then the greater is the partition of the dye in favour of the fibre phase (ie $[D]_f > [D]_s/L$) and the greater is the extent of dye uptake onto the substrate. In this context, because of the term $[D]_s/L$, it is evident that liquor ratio impacts directly on the amount of dye in solution rather than on the amount of dye in the fibre. Eq 6 predicts that values of $[D]_s$ will fall as liquor ratio decreases and, therefore, values of $[D]_f$ will increase accordingly, because values of L decrease with increasing liquor ratio (eg value of L @ a given liquor ratio: 0.2 @ 1:5; 0.1 @ 1:10; 0.02 @ 1:50). It follows that Eq 6 suggests the final partition of the dye between the fibre and solution phases is determined by the effect of liquor ratio on the amount of dye in solution.

Owing to the term ($[D]-[D]_s/L$ / $[D]_s/L$) in Eq 6, the degree of dye-fibre substantivity, as represented by the substantivity coefficient, S, is determined by the amount of dye in the bulk dyebath dye solution, $[D]_s$ relative to the total amount of dye within the dyeing system, $[D]$; the greater this difference, the higher is dye-fibre substantivity, and, therefore, the greater is dye uptake. As such, Eq 6 predicts that the solubility of the direct dye in the dyebath has a marked effect upon the substantivity coefficient, S, of the dye, owing to the term ($[D]-[D]_s/L$ / $[D]_s/L$), insofar as the substantivity of the dye (as reflected by S) will increase with decreasing liquor ratio (ie increasing values of *L*), as is observed in practice, because the amount of dye in solution, $[D]_{s,}$ decreases with decreasing liquor ratio owing to the relationship ($[D]_s/L$); hence, the partition of the dye will shift towards the fibre phase, $[D]_f$.

Eq 6 therefore provides an explanation for the nature of direct dye-cellulosic fibre substantivity based on the role of dye solubility, since the model relates the degree of substantivity displayed by the direct dye towards the fibre and the corresponding extent of dye uptake achieved, to the solubility of the direct dye in the dyebath.

Whilst the concentration of dye in both the dyebath $[D]_s$ and fibre, $[D]_f$, phases, as well as the total amount of dye within the immersion dyeing system, *[D]*, at the end of the dyeing process are measured in mass per unit volume (eg g l^{-1}), the units of fractional liquor, *L*, ratio are mass per unit volume (eg g l^{-1}); it follows that owing to the term $S = [D] - [D]_s/L \;/\; [D]_s/L$ in Eq 6, substantivity coefficient has dimensions of mass per unit volume (eg gl^{-1}). This situation parallels that described above (section 1.2.1) in the case of the theoretical model that invoked the concept of interstitial water in dyeing. Indeed, the similarity between Eq 6 and Eq 2 is clearly apparent.

It was demonstrated that the use of Eq 6 enabled experimental data obtained for the effects of both added electrolyte and reduced liquor ratio on the final uptake of direct dyes on cellulosic materials to be analysed from the viewpoint of establishing the mechanism by which added electrolyte and reduced liquor ratio promote dye uptake (3). In this context, the promotional effect imparted by reduced liquor ratio shown in Figure 8 can therefore be explained in terms of the partition of dye described by Eq 6.

Within a dyebath of given liquor ratio that contains added electrolyte, the extent to which dye uptake is promoted will be determined by the prevailing relative contributions of the added electrolyte and liquor ratio towards dye-fibre substantivity, and therefore, via Eq 6, to the distribution of dye between the aqueous and fibre phases, as described by the substantivity coefficient, *S*. As a constant concentration of added NaCl was employed in this work, it follows, that unlike electrolyte concentration, liquor ratio is a dyebath variable. Because the promotional effect imparted to dye uptake by the added NaCl was constant (as furnished by the use of 20 gl^{-1} NaCl), irrespective of the particular liquor ratio selected, then the level of dye-fibre substantivity achieved will be determined primarily by liquor ratio. Thus, the influence of liquor ratio on the substantivity coefficient, *S*, and, therefore, on the driving force for dyeing (ie its effect on increased dye aggregation and reduced dye solubility in the dyebath) will be much lower at high liquor ratios (eg 1:50, 1:20) than that which prevails at low liquor ratios (eg 1:3, 1:2), as was indeed observed (Figure 8), insofar as *S* decreases markedly with increasing liquor ratio in the case of dyeings undertaken in the presence of added NaCl.

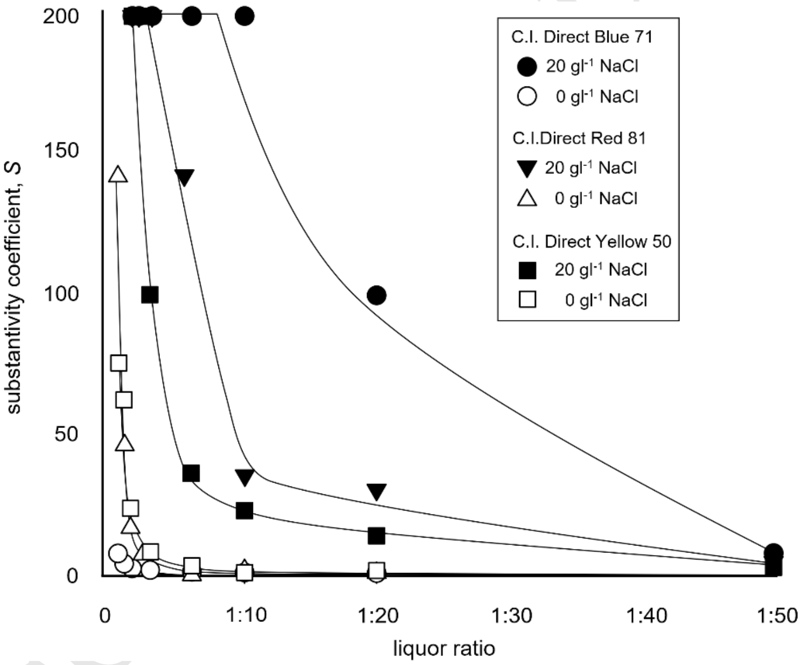


Figure 8 substantivity coefficient as a function of liquor ratio calculated using Eq 6; absence and presence of 20 gl^{-1} NaCl

It is also apparent from Figure89 that for dyeings which had been carried out in the absence of added inorganic electrolyte, a similarly dramatic reduction in substantivity coefficient attended a decrease in the liquor ratio used for dyeing. Indeed, each of the six curves shown in Figure 8 display similar negative exponential variance of *S* as a function of liquor ratio: the difference between the plots is that higher S values were recorded for dyeings which had been carried out in the presence of added NaCl.. Figure 8 therefore shows that the promotional effect of liquor ratio on dye-fibre substantivity, as predicted by Eq 6, decreases, exponentially, with increasing liquor ratio, irrespective of the presence or absence of added NaCl. In addition, Eq 6 predicts that reduced liquor ratio and added inorganic electrolyte exert a combinatorial effect on dye uptake in that Figure 8 clearly shows that at a given liquor ratio, the addition of 20 gl^{-1} NaCl to the dyebath enhances dye-fibre substantivity and, that this combinatorial promotional effect decreases with decreasing liquor ratio, as was depicted by the data shown in Figure 8.

If the proposal (3) that the sequential effects of increased dye aggregation and reduced dye solubility are responsible for the promotion of dye uptake imparted by both added electrolyte and lowered liquor ratio, it follows that the partition of the dye between the fibre and dyebath phases should favour the substrate in the presence of added electrolyte. This is demonstrated by the substantivity coefficient plot presented in Figure 9 wherein, according to Eq 6, a plot of D_f as a function of D_s/L provides values of S. It is apparent that higher values of S were obtained for dyeings that had been carried out in the presence of added electrolyte. The reduced solubility of the dye that results from electrolyte-induced dye aggregation in the dyebath will also be favoured should self-association of the dimers, trimers, etc. occur under appropriate conditions, such as dyeing at low liquor ratio. In effect, decreasing the liquor ratio augments the inherent tendency of the direct dyes to aggregate in the dyebath, which reduces the solubility of the dye in the dyebath and results in increased dye uptake. This means that the substantivity coefficient should increase as a consequence of reduced liquor ratio, as illustrated by the previous plot of substantivity coefficient, S, as a function of liquor ratio presented in Figure 8, which revealed that the magnitude of the coefficient obtained for the three dyes increased markedly with decreasing liquor ratio even when a constant concentration of added electrolyte (ie 20 gl^{-1} NaCl) had been used for dyeing.

Although in Figure 9, all values of S lie on the same straight line, irrespective of liquor ratio and absence/presence of electrolyte, as we are dealing with a dyeing system that contains a fixed amount of dye (ie 2% omf), the magnitude of *S* secured for each liquor ratio will vary according to the level of dye-fibre substantivity in operation, as described earlier. Consequently, dyeings produced under high dye-fibre substantivity conditions (ie in the presence of added electrolyte and at low liquor ratios) which have high values of substantivity coefficient, should be situated in the top left region of the straight line in Figure 9 whilst dyeings obtained under low dye-fibre substantivity conditions (ie in the absence of electrolyte and at high liquor ratios) will have lower *S* values and should be located in the bottom right region of the straight line shown in Figure 9, as observed.

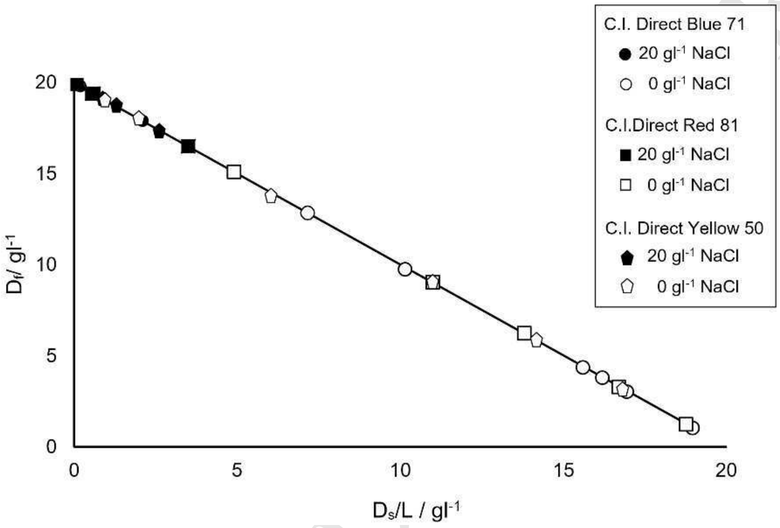


Figure 9 D_f as a function of D_s/L; absence and presence of 20 gl^{-1} NaCl

Thus, both the addition of electrolyte and reduction of liquor ratio exert the same promotional influence on dye uptake, since adding NaCl and lowering the liquor ratio have the same effect, namely that of encouraging dye aggregation in the dyebath, which reduces the solubility of the direct dye in the dyebath, which, in turn, favours increased dye uptake.

3.4.2 comparison of low liquor ratio/zero added electrolyte and high liquor ratio/added electrolyte dyeing

As discussed, commercial application processes for applying direct dyes to cotton and other cellulosic fibres manipulate the level of dye-fibre substantivity within the dye-electrolyte-fibre system so as to secure uniform dyeings of the required colour strength. This is achieved by using a particular amount of added inorganic electrolyte in combination with a particular liquor ratio, so that the relative contributions of the electrolyte and liquor ratio towards dye-fibre substantivity are controlled.

This is illustrated by the results displayed in Figure 6 which show that the extent of dyebath exhaustion achieved for dyeings that were carried out using low liquor ratios in the absence of added electrolyte were similar to those secured for dyeings that had been carried out using higher liquor ratios in the presence of added NaCl. Thus, both the addition of electrolyte and reduction of liquor ratio increased the substantivity of the direct dyes towards the cellulosic fibre and, therefore, the mechanism by which such enhanced dye-fibre substantivity accrues is likely the same for both electrolyte addition and reduced liquor ratio, namely, reduced solubility of the direct dye in the dyebath. Whilst dye aggregation can be expected to occur as a consequence of both the addition of electrolyte and reduction of liquor ratio, the contribution that dye aggregation makes, in each case, towards reduced dye solubility (and thus increased dye-fibre substantivity) will vary according to the liquor ratio and amount of electrolyte employed. In this context, it follows that a given amount of added electrolyte will be more effective in promoting dye uptake at higher liquor ratios, as was indeed observed in this work (Figures 7 and 8).

Furthermore, since the mechanism by which dye-fibre substantivity is promoted is essentially the same for both electrolyte addition and reduced liquor ratio, it follows that the combination of these two effects will result in greatly enhanced dye-fibre substantivity and the attendant risk of unlevel dyeing. As discussed in section 3.1, in this work, unlevel dyeings were obtained in the presence of added electrolyte using a liquor ratio of 1:1. That such unlevelness is attributable to very high dye-fibre substantivity promoted by excessive dye aggregation coupled with greatly reduced dye solubility, bears support from the findings that level dyeings were achieved in the absence of added electrolyte when dyeing was undertaken using a 1:1 liquor ratio. It can be proffered that level dyeing was achieved in the absence of, rather than in the presence of, added electrolyte because dye-fibre substantivity was lower in the electrolyte-free dyeing system.

In the case of dyeings carried out in the presence of added NaCl, the findings (Figure 6) that dye exhaustion was greatest in the case of dyeings that were obtained using the lowest liquor ratios can be attributed to the high dye-fibre substantivity that arose from the combination of added electrolyte and low liquor ratio. However, this particular trend of increased dye exhaustion as a function of decreasing liquor ratio in the presence of added electrolyte was not reflected in the corresponding values of colour strength achieved (Figure 5). Clearly, colour strength decreased at low liquor ratios which suggests that whilst the high substantivity conditions that prevailed at low liquor ratios in the presence of NaCl encouraged dye exhaustion, diffusion of the adsorbed dye molecules within the cotton may have been impaired because of excessive aggregation/reduced dye solubility.

Although the above discussion relates the extent of dye aggregation in the dyebath to the solubility of the direct dye in the dyebath, in the context of the well-known marked propensity of direct dyes to aggregate in solution, it is of course possible that either a decrease in liquor ratio and/or addition of electrolyte may reduce dye solubility without necessarily encouraging dye aggregation. However, the inter-relationships between the nature of direct dye aggregation and its relationship to the structure of the dyes, their predisposition to aggregate in solution and the nature of the aqueous dyebath, are not well enough understood at the present time to resolve this issue.

Although the three dyes used in this work are azo compounds, they are structurally diverse and contain either two sulfonate groups (C.I. Direct Red 81) or four sulfonate groups (C.I. Direct Blue 71 and C.I. Direct Yellow 50). It is evident from Table 1 and Figures 5 and 6 that the three dyes varied, in absolute terms, from the perspectives of colour strength and levels of dye exhaustion obtained, when applied in the presence of added electrolyte, which was expected, in view of the previously mentioned dye structure-dependency of the dyeing behaviour of individual direct dyes; indeed, such differences in dyeing behaviour were anticipated in view of the SDC classification system for direct dyes. However, the three dyes displayed noteworthy similarity in their response to liquor ratio variation when applied in the presence of added NaCl, as exemplified by the dye exhaustion results displayed in Figure 6. This suggests that variation in dye structure and sulfonate group content contributed relatively little towards dyeing behaviour in the presence of a (fixed) amount of added electrolyte.

In terms of controlling the level of dye-fibre substantivity within the direct dye-electrolyte-fibre system by using a particular amount of added inorganic electrolyte in combination with a particular liquor ratio, Figure 10 shows, in the case of the dyeings obtained in the absence of added 20 gl^{-1} NaCl using both 1:1 and 1:1.5 liquor ratios, that the colour strength of dyeings using both C.I. Direct Red 81 and C.I Direct Yellow 50 were of similar magnitude to those secured for dyeings which had been produced using 1:10, 1:20 and 1:50 liquor ratios in the presence of added electrolyte, and, in the case of C.I. Direct Blue 71, were only slightly lower than those obtained at the higher liquor ratios in the presence of added electrolyte. These findings support the proposition that the addition of electrolyte and reduction of liquor ratio impart the same promoting effect on dye uptake.

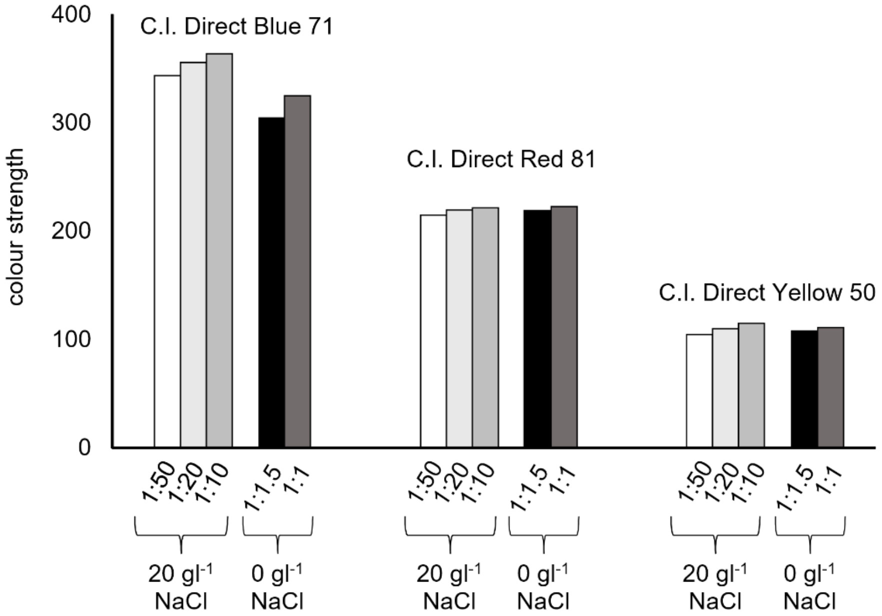


Figure 10 colour strength as a function of liquor ratio; absence and presence of 20 gl^{-1} NaCl

Indeed, the results obtained in this work, as illustrated by the data presented in Figure 10, indicate that for each of the three, arbitrarily selected commercial direct dyes used in this study, level dyeings can be obtained at very low liquor ratio (1:1.5 and 1:1) in the absence of added inorganic electrolyte.

Thus, the concerns that often are associated with the use of low liquor ratios in exhaust dyeing, namely that difficulties can be experienced in controlling dye migration and, thus, in securing level dyeings, are a consequence of a lack of understanding of the combined effects which liquor ratio and added electrolyte exert upon dye uptake. This work has shown that consistently level dyeings can be obtained at very low liquor ratios, so long as the promotional effect imparted by added electrolyte is negated. Furthermore, the depth of shade of the added electrolyte-free dyeings obtained at such low liquor ratios demonstrate that the immersion dyeing of cotton can be carried out using commercial direct dyes in the complete absence of added electrolyte.

3.5 effect of diluent electrolyte

Commercial dyes were used in this work so as to reflect commercial dyeing practice. However, commercial direct dyes usually contain significant quantities of shading components and diluents, the latter often including inorganic electrolyte such as NaCl, which are added to the dye by the manufacturer as part of dye standardisation. For example, it was reported (22) that the amount of added standardising constituents ranged from 53% to 74% in the case of eight commercial direct dyes. In terms of the three direct dyes employed in this work, conductivity and chloride-specific, ion-selective electrode determinations revealed that the amount of diluent NaCl present in the commercial samples was: C.I. Direct Blue 71 8.3%, C.I. Direct Red 81 29.5% and C.I. Direct Yellow 50 6.5%. Details of the two techniques that were used to determine the electrolyte content of the dye samples are discussed in a subsequent part of the paper.

Whilst a constant amount of each of the three direct dyes was applied to the cellulosic substrate (ie 2% on mass of fibre) irrespective of the liquor ratio used for dye application, the dye concentration in the dyebath at the start of dyeing will have varied, according to the liquor ratio employed. Indeed, as the initial dye concentration within the dyebath increased by a factor of ~33, based on liquor volume, over the 1:50 to 1:1.5 liquor ratio range used (ie 0.4 g l^{-1} @ 1:50; 1 gl^{-1} @ 1:20; 2 g l^{-1} @ 1:10; 3.3 gl^{-}

^{1} @ 1:6; 6.6 gl^{-1} @ 1:3; 10 gl^{-1} @ 1:2, 13.3 gl^{-1} @ 1:1.5), then the concentration of diluent NaCl in the dyebath derived from the commercial direct dye sample, will have varied similarly, over the same range of liquor ratio, based on liquor volume. Thus, the presence of diluent NaCl in the dyebath may have contributed to the observed increase in both dye exhaustion (Figure 6) and colour strength (Figure 5) that accompanied a decrease in liquor ratio; this possible situation was investigated as discussed below.

3.5.1 dyeing in the absence of added electrolyte

Figure 11 shows the colour strength of dyeings achieved at liquor ratios of 1:50 to 1:1.5, as a function of initial dye concentration for each dye used in the absence of 20 gl^{-1} added NaCl. It is apparent that an increase in initial dye concentration over the range 0.4 to 3.3 gl^{-1} (corresponding to liquor ratios of between 1:50 to 1:6) resulted in a sharp increase in colour strength and that further increase in initial dye concentration over the range 6.6 to 20 gl^{-1} (corresponding to liquor ratios of 1:3 to 1:1) was accompanied by a more gradual increase in colour strength. As the shape of the curves obtained for the three dyes used were reasonably similar, it appears that the effects observed were not dye-specific. The results in Figure 11 concur with those displayed in Figure 5, which show that in the absence of added NaCl, colour yield increased with decreasing liquor ratio over the complete range of liquor ratios examined (ie 1:50 to 1:1), for each of the three dyes studied.

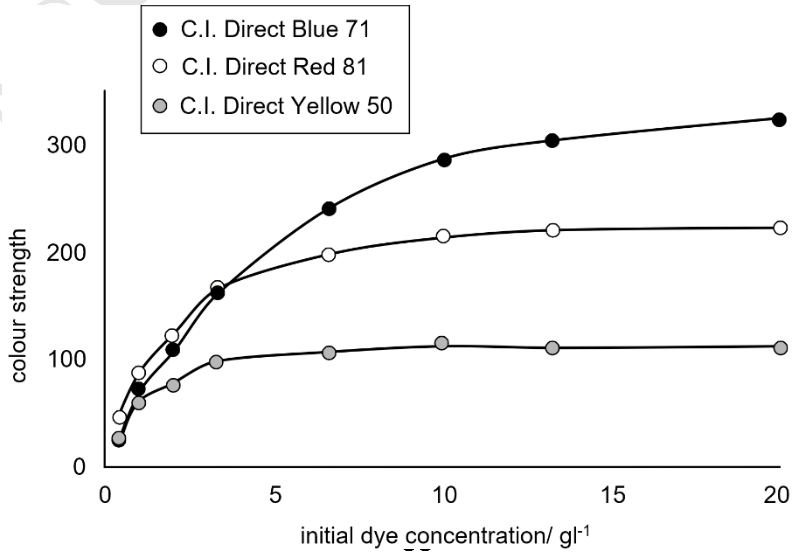


Figure 11 colour strength as a function of initial dye concentration; absence of NaCl

If diluent NaCl present in the commercial dye samples contributed to the promotional effect of reducing liquor ratio on dye uptake then in the absence of 20 gl^{-1} added NaCl, colour strength should increase with increasing initial dye concentration, because the amount of diluent inorganic electrolyte in the dyebath derived from the dye, would also increase. However, the curvilinear plots displayed in Figure 11 and, also, the marked difference in the rates of increase in colour strength that occurred prior to and after an initial dye concentration of 3.3 gl^{-1} (corresponding to a liquor ratio of 1:6), warrant examination.

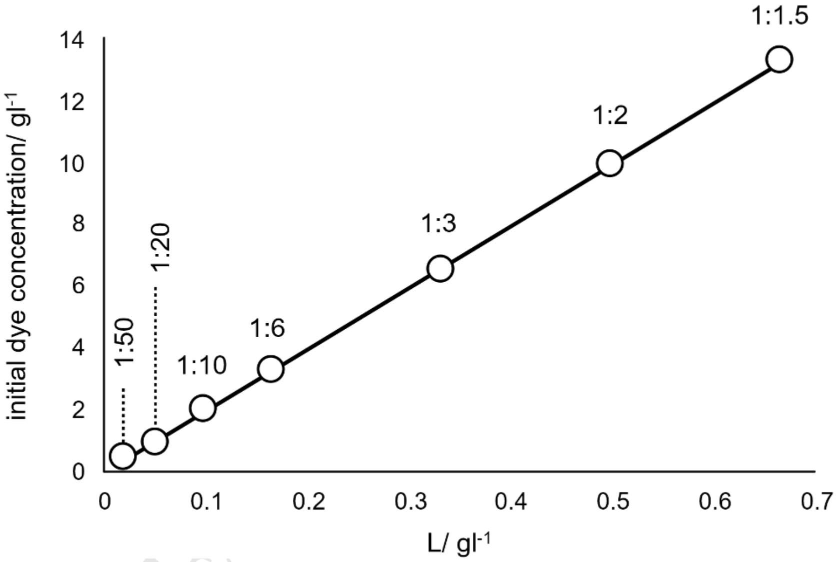


Figure 12 initial dye concentration as a function of fractional liquor ratio

As liquor ratio is a fraction (eg 1/20, 1/10, etc.) then liquor ratio can be expressed mathematically by the fractional liquor ratio, *L* (units = mass/volume, such as gl^{-1}). As mentioned, values of *L* increase with decreasing liquor ratio: for example, *L* increases from 0.01 in the case of a 1:100 liquor ratio, through 0.02 for a liquor ratio of 1:50, 0.1 for a 1:10 liquor ratio and 0.2 for a liquor ratio of 1:5. When values of initial dye concentration are plotted as a function of fractional liquor ratio, an essentially linear relationship is obtained (Figure 12; the various liquor ratios that correspond to the values of *L* are displayed in the figure).

Thus, according to Figure 12, the concentration of diluent NaCl in the dyebath derived from the commercial direct dyes should be expected to increase in an identical linear manner as a function of liquor ratio, from which it follows that if diluent electrolyte present in the dye contributes to the observed promotion of colour strength imparted by a reduction in liquor ratio (Figure 11), the extent of this contribution should be proportional to the amount of diluent electrolyte present within the dyebath that is derived from the dye. However, the curvilinear relationship observed for the variation in colour strength as a function of initial dye concentration (Figure 11) does not correlate with the likely linear variation of diluent NaCl concentration as a function of liquor ratio (Figure 12).

In this context, the observed sharp increases in colour strength that attended an increase in initial dye concentration over the range 0.4 to 3.3 gl^{-1} and the subsequent more gradual increase in f_k values over the subsequent initial dye concentration range 6.6 to 20 gl^{-1} (Figure 11) suggest that any promotional effect exerted by diluent NaCl in the dyebath derived from the dye differs, according to whether dyeing had been carried out at high liquor ratios (ie between 1:50 and 1:6) or at low liquor ratios (ie 1:3 to 1:1). This finding can be explained by considering that the extent to which dye uptake is enhanced by added electrolyte and reduced liquor ratio will be greatest when the promotional impacts of reduced liquor ratio and added NaCl are maximised (ie using low liquor ratios in the presence of added electrolyte) and will be lowest when the promotional impacts of reduced liquor ratio and added electrolyte are minimised (ie using high liquor ratios in the absence of added NaCl).

Thus, for the observed variation of colour strength as a function of initial dye concentration (Figure 11), at higher liquor ratios (ie between 1:50 and 1:6) and, therefore, low values of initial dye concentration (ie between 0.4 and 3.3 gl^{-1}), the sharp increase in colour strength that accompanied an increase in initial dye concentration (ie a decrease in liquor ratio) may be attributable to the additional promotional effect on dye uptake exerted by the increasing diluent NaCl concentration. In other words, the intrinsically low substantivity of the high liquor ratio dyeing systems (ie liquor ratios of between 1:6 and 1:50) in the absence of added NaCl may have been increased markedly by the presence of increasing concentrations of diluent electrolyte. Hence, the inherently low dye-fibre substantivity provided by the use of high liquor ratios in conjunction with zero added NaCl, was augmented by the presence of diluent electrolyte in the dyebath.

However, the more gradual increase in colour strength that occurred at lower liquor ratios of 1:3 to 1:1, which corresponded to an increase in initial dye concentration over the range 6.6 to 20 gl^{-1} (Figure 11), implies that the presence of increasing concentrations of diluent electrolyte had comparatively less influence on the higher levels of dye-fibre substantivity that prevailed at these liquor ratios. In other words, diluent NaCl imparted only moderate increases in the intrinsically high dye-fibre substantivity dyeing system that prevailed at low liquor ratios.

Furthermore, the plots in Figure 11 suggest that the particular concentration of diluent electrolyte in the dyebath conferred by the presence of 3.3 gl^{-1} dye (ie at a 1:6 liquor ratio), may be of significance in terms of the combined promotional effects on dye uptake of liquor ratio and added diluent electrolyte. The possible reasons as to why, at initial dye concentrations <3.3 gl^{-1} (ie from 1:50 to 1:6 liquor ratio) diluent electrolyte played a far more significant role in promoting dye uptake than when initial dye concentrations >3.3 gl^{-1} (ie at liquor ratios from 1:6 to 1:1) were used, merits discussion.

3.5.2 dyeing in the presence of added electrolyte

The plots of colour strength as a function of initial dye concentration for dyeings obtained in the presence of 20 gl^{-1} NaCl (Figure 13) differ in shape to those obtained in the absence of added electrolyte (Figure 11). After a gradual increase in colour strength over the initial dye concentration of 0.4 to 3.3 gl 1 (corresponding to liquor ratios of 1:50 to 1:6), the f_k values decreased gradually with further increase in initial dye concentration from 6.6 to 13.3 gl^{-1} (corresponding to liquor ratios of 1:3 to 1:1.5.

In view of the above discussions concerning the possible effects of diluent electrolyte on the values of f_k obtained in the absence of added NaCl (Figure 11), the gradual increase in colour strength observed over the initial dye concentration range 0.4 to 3.3 gl^{-1} when dyeing had been undertaken in the presence of added electrolyte (Figure 13) may have arisen from the diluent NaCl having contributed towards increased dye uptake, because the concentration of diluent electrolyte in the dyebath derived from the dye also will likely have increased over the same range of liquor ratio.

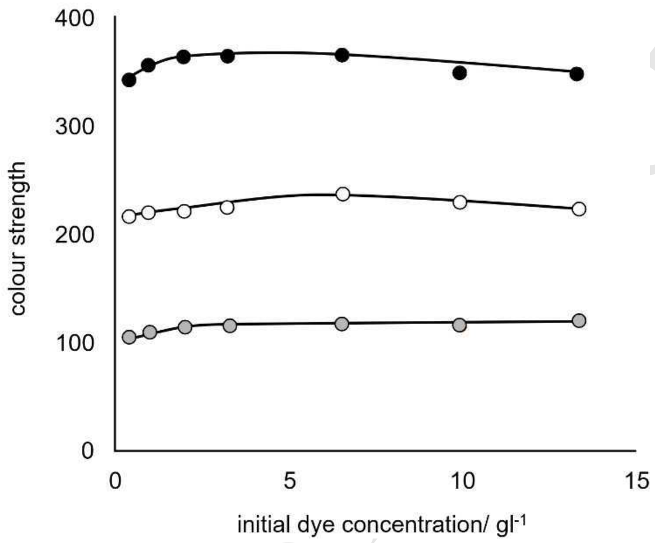


Figure 13 colour strength as a function of initial dye concentration; presence of 20 gl^{-1} NaCl

Thus, over the initial dye concentration range 0.4 to 3.3 gl^{-1}, which corresponded to liquor ratios of between 1:50 and 1:6, the promotional effect imparted by the increasing diluent NaCl concentration may have been of greater magnitude than that provided by reduction in liquor ratio. However, a comparison of Figures 11 and 13 reveals that the magnitude of the possible promotional effect of the diluent at liquor ratios of 1:50 to 1:6 was much lower when dyeing had been carried out in the presence of added NaCl.

Nonetheless, in the presence of a constant concentration of added NaCl (ie 20 gl^{-1}), the levels of dye-fibre substantivity that prevailed at liquor ratios between 1:50 and 1:6 may have been sufficiently low enough to be boosted by the presence of diluent electrolyte derived from the commercial dye. Thus, the diluent electrolyte in the dyebath may have provided increased dye-fibre substantivity which augmented the intrinsically low dye-fibre substantivity provided by the use of high liquor ratios, even in the presence of added NaCl.

However, the ensuing very gradual decrease in colour strength observed for lower liquor ratios (Figure 13), namely over the range 1:3 to 1:1.5, which corresponded to increasing initial dye concentrations of 6.6 to 13.3 gl^{-1}, suggests that in the presence of added NaCl, the levels of dye-fibre substantivity secured at these lower liquor ratios (ie between 1:3 and 1:1.5) were inherently high and the presence of (additional) diluent NaCl may well have initiated excessive dye aggregation and reduced dye solubility that resulted in reduced in dye uptake. Since it is assumed that reduction of liquor ratio and addition of electrolyte convey the same promotional effect on direct dye uptake, then the extent to which diluent electrolyte may have enhanced the intrinsically very high dye-fibre substantivity provided by the use of low liquor ratios in conjunction with 20 gl^{-1} added NaCl was such that dye uptake was reduced, owing to excessive dye aggregation and reduced dye solubility.

A comparison of the plots displayed in Figures 11 and 13 reveals that similar behaviour was obtained in both the absence and presence of added NaCl for each of the three dyes used, which implies that the results were not dye-specific, but, rather, were dye-system specific (ie dye-fibre or dye/electrolyte/fibre). It therefore seems reasonable to suggest that irrespective of whether dyeing had been carried out in the absence or presence of added electrolyte, diluent NaCl present in the commercial dyes used in this work may have exerted a promotional effect on dye uptake. However, the magnitude of this enhanced dye uptake decreased markedly with decreasing liquor ratio and that any contribution towards dye uptake promotion imparted by diluent electrolyte was considerably less effective at very low liquor ratios.

In order to fully resolve the possible influence of diluent electrolyte on dye uptake, especially at low liquor ratios, a future part of this paper will present the findings of a study of the exhaust application of pure dyes that were free of all diluent.

4. Conclusions

Both the colour strength of 2% omf dyeings on cotton and the extent of dye exhaustion achieved for the three commercial direct dyes were promoted by the addition of 20 gl^{-1} NaCl at each of the liquor ratios employed.

The observed promotion of dye uptake and colour strength imparted by both added electrolyte and reduced liquor ratio were interpreted in terms of their effects on the substantivity of the direct dyes towards the cotton fibre. It seems likely that the addition of inorganic electrolyte and reduction of liquor ratio impart the same promoting effect on dye uptake, as the two, ostensibly disparate acts of adding electrolyte to an aqueous dyebath and reducing the liquor ratio used in dyeing, have the same result, namely that of encouraging dye aggregation in the dyebath, which reduces the solubility of the direct dye in the dyebath, which, in turn, increases the concentration gradient between the amount of dye in solution the dyebath and fibre phases and results in increased dye uptake. As such, these findings concur with the theoretical models, based on the concept of interstitial water, that were proposed to explain the roles of added NaCl or Na_2SO_4 (3) and reduced liquor ratio in the application of direct dyes to cotton.

Irrespective of whether dyeing is undertaken in the absence or presence of added electrolyte, diluent electrolyte present in the commercial dyes may exert a promotional effect on dye uptake, although the magnitude of this enhanced dye uptake decreases markedly with decreasing liquor ratio.

The results clearly show that for each of the three commercial direct dyes used, level dyeings can be obtained at very low liquor ratio (1:1.5 and 1:1) in the complete absence of added inorganic electrolyte. The findings reveal that the models (3, 4) can be used to explain why it is possible to dye cotton to realistic depths of shade using direct dyes in the complete absence of added inorganic electrolyte.

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