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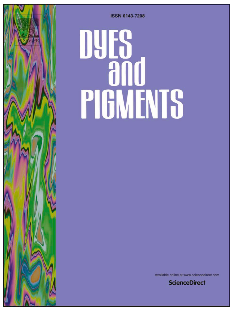

The role of auxiliaries in the immersion dyeing of textile fibres: Part 4 theoretical model to describe the role of liquor ratio in dyeing cellulosic fibres with direct dyes in the absence and presence of inorganic electrolyte

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The role of auxiliaries in the immersion dyeing of textile fibres: Part 4 theoretical model to describe the role of liquor ratio in dyeing cellulosic fibres with direct dyes in the absence and presence of inorganic electrolyte

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Abstract

A model is proposed to explain the manner by which the uptake of direct dyes on cellulosic fibres is promoted by a reduction in the liquor ratio used for dyeing. According to the model, which invokes the concept of interstitial water in dyeing, reducing the liquor ratio promotes dye aggregation which reduces the solubility of the dye in the bulk dyebath phase, so that the inherent preference of the dye to favour the aqueous phase shifts towards the fibre phase. It is suggested that the same mechanism accounts for the promotion of direct dye uptake imparted by the addition of inorganic electrolyte to direct dye dyebaths. As such, reduced liquor ratio and added inorganic electrolyte exert a combinatorial promotional effect on direct dye uptake.

Highlights

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

keywords

keywords: dyeing cotton; dyeing auxiliaries; electrolyte; direct dyes; liquor ratio

1 Introduction

A wide variety of different types of auxiliary chemical are routinely employed in the application of dyes to textile fibres using immersion dyeing processes. Such dyeing auxiliaries vary in terms of the nature of the functionality they provide to immersion dyeing processes, as well as both the environmental and financial aspects associated with their use (1). Despite their widespread usage, the precise mode of action of many auxiliaries has not been fully resolved.

In recognition of the global popularity of cotton and other cellulosic fibres, the previous two parts of the paper (2, 3) considered the role of the most important auxiliary used in the dyeing of cellulosic fibres, namely NaCl or Na_2SO_4. Although very large amounts of inorganic electrolyte are habitually added to direct dye dyebaths to promote dye uptake onto cellulosic fibres, the precise nature of the promotional effect imparted by NaCl or Na_2SO_4 has not been entirely resolved, despite considerable research interest over many decades. As conventional models of direct dye adsorption cannot adequately account for either the inherently low uptake of direct dyes on cellulosic fibres in the absence of added inorganic electrolyte nor the marked ability of NaCl and Na_2SO_4 to promote dye uptake, a theoretical model was proposed to explain the promotional effect of added inorganic electrolyte on the uptake of direct dyes on cellulosic fibres, which utilised the concept of interstitial water (3). According to this model, the inherently low substantivity displayed by direct dyes towards cellulosic fibres in the absence of added electrolyte is attributable to the dye's marked preference for the aqueous dyebath phase, which stems from the dye's high aqueous solubility. 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 intrinsic preference of the previously highly soluble dye to favour the aqueous phase shifts towards the fibre phase and so dye uptake is promoted.

In this part of the paper, the previously recounted theoretical model of the promotional effect imparted by added inorganic electrolyte on dye uptake (3) will be utilised to develop a model that seeks to explain the manner by which reducing the liquor ratio used for dyeing promotes the uptake of direct dyes on cellulosic fibres.

The next part of the paper describes how experimental results obtained by applying direct dyes to cotton can be interpreted using the two theoretical models that have been devised to describe the effects of added inorganic electrolyte and liquor ratio on direct dye uptake, so as to explain why it is possible to dye cotton (and other cellulosic fibres) using direct dyes employing an immersion process in the complete absence of added electrolyte at low liquor ratio. In this context, subsequent parts of the paper will demonstrate that the theoretical models enable commercially acceptable dyeings to be achieved in the complete absence of added inorganic electrolyte.

2 conventional models of direct dye adsorption on cellulosic fibres

As previously recounted (2, 3), the mechanism by which direct dyes are adsorbed onto cellulosic fibres is interpreted conventionally using Eq 1 (and equations based on this), which describes the partition of dye between the fibre phase and the solution phase when equilibrium dye uptake has been achieved (ie when dye adsorption and dye desorption processes are equal), 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.

$$K = \frac{[D]_f}{[D]_s} \qquad 1$$

The equilibrium partition coefficient, K, describes the distribution of the dye between the dyebath, s and fibre, f, phases; 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 the extent of dye uptake onto the substrate.

$$-\Delta\mu^o = RTln\frac{[Na^+]_f^z[D^-]_f}{V^{z+1}[Na^+]_s^z[D^-]_s} \qquad 2$$

Variants of Eq 1, such as Eq 2 (4), are widely used to express the partition of the dye between the fibre and solution phases at the end of equilibrium dyeing in terms of the thermodynamic standard affinity of the dye, $-\Delta\mu^{\theta}$ (5). However, the approach adopted in using equations such as Eq 2, suffers several shortcomings, as discussed previously (2, 3), insofar as it provides no meaningful information about the dyeing process prior to equilibrium, nor does it offer explanations as to why direct dyes display inherently low substantivity towards cellulosic fibres in the absence of added inorganic electrolyte or why NaCl or Na_2SO_4 are so effective in promoting dye uptake. Of relevance to this part of the paper, conventional models of direct dye adsorption on cellulosic fibres are unable to account for the promotional effect imparted by reduced liquor ratio on dye uptake.

As mentioned (3), the work described in this and the previous part of this paper does not seek to establish the mechanism of direct dyeing in terms of how the direct dye molecules interact with the cellulosic fibre, but, rather, aims to determine both the motivational force that drives the transfer of the direct dye molecules from the dyebath to the fibre and the role of liquor ratio in this transferal process under non-equilibrium conditions that are typically encountered in commercial immersion dyeing.

It is of interest to note that many of the findings of the various researchers referred to in both this and the previous part of this paper (3) were the result of meticulous, elegant and, at the time, transformational studies on dyeing. However, these observations were made when the liquor ratio employed for dyeing was not considered as being in any way problematic from either economic, technical or environmental perspectives, because, at the time, water was plentiful and (relatively) cheap; consequently, dyeing machines customarily operated at very long liquor ratios. Indeed, it wasn’t until the oil crises of 1973 and 1980 and the resulting increased costs of heating (as well as evaporating, pumping, etc.) the very large volumes of water that were habitually employed in exhaust dyeing processes, that both industrial practice and research effort began to focus on ways of reducing water usage and, therefore, liquor ratio became of major importance. Thus, the findings reported in many earlier studies concerning the effects of added electrolyte on direct dye adsorption often were obtained using very long liquor ratios (eg 1:40 or greater) and the crucially important combinatorial nature of the effects of added inorganic electrolyte and reduced liquor ratio on direct dye uptake received little, if any, attention.

3 liquor ratio

As discussed in the first part of this paper (1), the amount of water that is used in immersion dyeing is expressed in terms of liquor ratio, which describes the ratio of the amount of substrate used in relation to the amount of water used in dyeing. For example, a liquor ratio of 1:5 means that for every kg of fibre used in dyeing, 5 kg (≡ 5 l) is employed whilst 8 kg (≡ 8l) of water would be utilised in the case of a 1:8 liquor ratio having been selected for dyeing. Liquor ratio impacts upon several aspects of immersion dyeing processes, including dye migration and levelling, as well both the rate and extent of dye uptake and, in the case of reactive dyes on cellulosic fibres, the extent of dye-fibre fixation.

Table 1 Effect of liquor ratio on the extent of dye exhaustion on cotton; 2% omf dye; 98°C; no added inorganic electrolyte (6)

C.I. Direct	dye exhaustion/%		
	1:20	1:10	1:6
Blue 71	15.2	19.0	21.8
Red 81	16.5	31.2	45.2
Yellow 50	29.1	45.2	70.2

Liquor ratio has a pronounced effect on the uptake of direct dyes on cellulosic fibres [eg (7-10)] as shown by the data presented in Table 1; furthermore, liquor ratio influences the effectiveness with which added inorganic electrolyte promotes dye uptake.

The particular liquor ratio that is utilised in immersion dyeing varies according to, for instance, type of dye, type of fibre, fibre construction, machine type, etc. For example, contemporary jet dyeing machines used for knitted cotton fabrics typically employ a 1:8 – 1:10 liquor ratio whereas in the case of *Best Available Technology* (BAT) jet machines, a liquor ratio of 1:4.5 - 1:5 is common. Liquor ratio influences both the rate and extent of dye uptake, as well as the amount of auxiliaries that are employed, when dyeing recipes are based on liquor ratio rather than omf (1).

Although the influence of liquor ratio on dye uptake in immersion dyeing processes is a well-discussed topic, the precise manner by which a decrease in liquor ratio increases dye uptake has not been fully resolved, this being illustrated by the fact that the previously mentioned fact that the current lowest (ie BAT) liquor ratio employed commercially for the exhaust dyeing of knitted cotton fabric is between 1:4.5 and 1:5. That ultra-low liquor ratios of 1:1 to 1:2 are not currently utilised for the immersion dyeing of cellulosic fibres with anionic dyes can be attributed to an inadequate understanding of both the precise mechanism by which liquor ratio controls dye uptake in exhaust dyeing processes and the role of added electrolyte in immersion dyeing processes for cellulosic fibres. Since, in this work, the effects on direct dye uptake of both liquor ratio and added electrolyte are examined and interrelated, the nature of the relationship between liquor ratio and dye uptake warrants examination.

Because liquor ratio determines the amount of water that is employed in immersion dyeing processes, it seems apposite to briefly consider the role of water in such dyeing process.

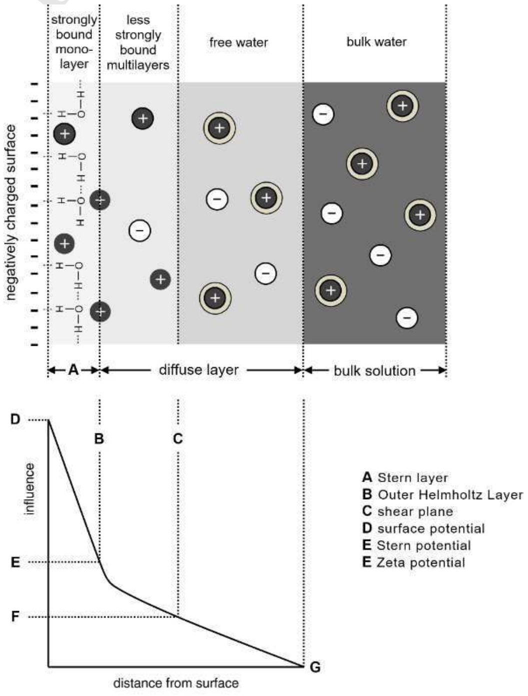


Figure 1 simplified representation of the coincidence of electric double layer and the concept of free and bound water (3)

It has been proposed (3) that different types of sorbed water are present within textile substrates, namely, strongly bound, less strongly bound and free water and that such a model has strong resonance with current views of electrical double-layer theory (Figure 1).

Owing to the presence of both immobile bound water molecules and reduced mobility bound sorbed water molecules, coupled with the influence of the charged textile fibre surface on the distribution of sorbed ions and molecules within the substrate, it was proffered (3) that both electric double-layer theory and the concept of free and bound sorbed water predict that the ionic environment of an aqueous solution that is in close proximity to a charged surface, such as a textile fibre, will differ markedly to that which exists in the surrounding bulk aqueous solution.

4 a model to explain the effect of liquor ratio on the adsorption of direct dyes on cellulosic fibres

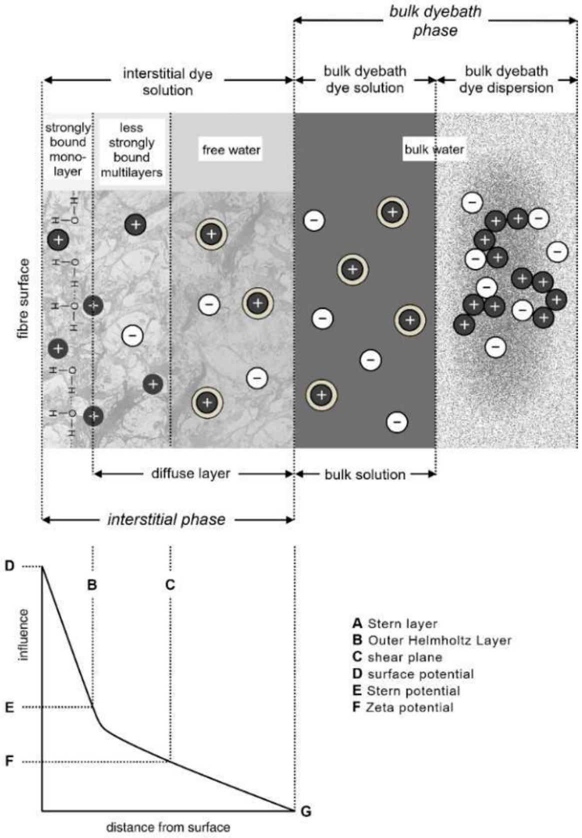


Figure 2 simplified representation of the coincidence of interstitial water, electric double layer and the concept of free and bound water (3)

Based on the above notion that different types of sorbed water are present within textile substrates, it was suggested (3) that the water which is adsorbed by a fibrous substrate during aqueous immersion dyeing processes is located within the interstices of the substrate. In accordance with electric double-layer theory and the concept of free and bound sorbed water molecules, such interstitial water will differ to that which resides within the surrounding bulk dyebath because of the influence of the charged fibre surface and that of both the immobile and reduced mobility bound water molecules on the distribution of sorbed ions/molecules (Figure 2).

4.1 interstitial water

According to the concept of interstitial water, which has previously been invoked in the development of an immersion dyeing process (7) and a wash-off process for dyeings (8-11), interstitial water provides functions that differ to those afforded by the remaining bulk water, such as heating, agitation, etc. that are required for immersion dyeing. The volume of interstitial water present within a textile substrate can be assumed to correspond to the moisture regain of the substrate at 100% Relative Humidity, *RH*, which, by way of example, in the case of cotton, corresponds to 0.22 l kg^{-1} (11).

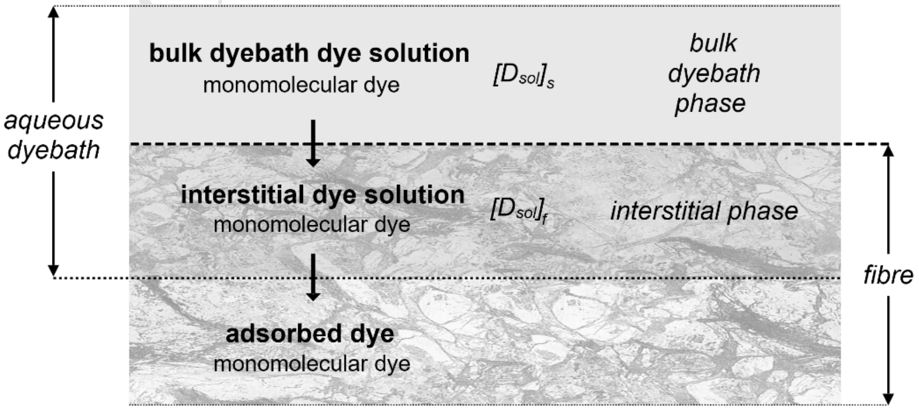


Figure 3 representation of interstitial dyeing mechanism (3)

A mechanism was proposed (3) to explain the adsorption of direct dyes on cellulosic fibres based upon the concept of interstitial water, which is depicted in Figure 3. According to this mechanism, the aqueous dyebath comprises both interstitial water that resides within the wetted, swollen fibre as well as bulk dyebath water that surrounds the substrate. As the interstitial water (which corresponds to ~22% of the fibre mass in the case of cotton) comprises dyebath solution which is an integral component of and, therefore, is in intimate contact with, the swollen substrate, the transfer of dye molecules from the dyebath to the fibre (ie the process of dyeing) takes place within the water that is present in the fibre interstices.

The transfer of dye molecules from the bulk dye solution in the dyebath to the solid fibre occurs via an interstitial dye solution that is present within the substrate. At the start of dyeing, it is envisaged (Figure 3) that the aqueous dyebath comprises both an interstitial phase and a bulk dyebath phase; both phases contain dissolved dye molecules. Dye molecules within the interstitial dye solution are able to interact with the fibre and become adsorbed, via a Freundlich or Langmuir mechanism (5). Dye molecules in the bulk dyebath solution then transfer to, and, thereby, replenish the interstitial dye solution from which the adsorption of further dye molecules on the substrate can occur. The process of dye transfer from the bulk dyebath dye solution to the interstitial dye solution, followed by dye adsorption on the fibre, as represented by Figure 3, continues until either the fibre is saturated with dye or all of the dye has been adsorbed.

Thus, only a relatively small proportion of the water that is utilised in immersion dyeing is directly involved in (and required for) the transfer of dye from the dyebath to the substrate and, therefore, the remaining vast majority of the water that is employed in conventional exhaust dyeing processes provides other functionality, such as heating, fibre agitation, etc. As liquor ratio expresses the ratio of the amount of water used in dyeing to the amount of fibre, then, because the amount of interstitial water within the fibre is constant (ie ~0.22 l kg^{-1} in the case of cotton), it follows that the proportion of water present in the interstices of the substrate (ie that which is directly utilised in dye transfer) relative to the total amount of water used for dyeing, decreases markedly, with increasing liquor ratio.

For example, using a moisture regain value of 0.22 l kg-1 for cotton, 22% of the total dyebath volume is directly involved in the process of dye transfer to the substrate (ie dye adsorption), which means that the remaining ~78% provides additional functionality, which corresponds to 3.9 l in the case of a 1:5 liquor ratio, 7.8 l for a 1:10 liquor ratio and a considerable 39 l if a 1:50 liquor ratio is employed for dyeing. Thus, a large excess of water is customarily utilised in conventional immersion dyeing processes which increases with increasing liquor ratio.

In a subsequent part of the paper, the crucial role of interstitial water in immersion dyeing processes will be considered and it will be demonstrated that the only water that is required to achieve dye adsorption during immersion processes is that which resides within the interstices of the substrate, with the result, that acceptable levels of dye uptake, colour strength and uniform dyeings can be secured using liquor ratios <<1:1 for a range of different classes of dye on various types of textile fibre.

4.2 the roles of dye diffusion and dye-fibre substantivity in direct dye adsorption

As recounted (3), a major contributory factor in the transfer of dye molecules from the dyebath to the fibre during dyeing is the inherent driving force that is provided by diffusional movement of the dye down the dye concentration gradient that exists between the dyebath phase and the fibre phase. In essence (3), owing to the high dye concentration gradient that exists at the start of dyeing, when a fibre is placed in an aqueous dyebath, dye molecules move spontaneously from the dyebath to the fibre. Dye uptake proceeds until either an equilibrium is established between the amounts of dye present within the two phases or all of the dye has transferred to the fibre phase, which is the preferred situation in the case of commercial immersion dyeing processes.

In exhaust dyeing, the amount of dye used is calculated on the basis of the mass of the fibre (eg 2% omf) rather than on liquor ratio (eg 20 gl^{-1}). Consequently, if a given mass of fibre is dyed employing two different liquor ratios, then even though the mass of fibre is constant, the effective concentration of the dye in the dyebath will vary, according to the particular liquor ratio employed. For example, consider the application of a direct dye that is deployed at 5% omf in a process for dyeing 250 kg of fibre. If a 1:10 liquor ratio is used for dyeing, then at the start of dyeing, the concentration of dye in the dyebath would be 5 gl^{-1} whereas at a 1:5 liquor ratio, the dye concentration at the start of dyeing would be 10 gl^{-1}. Thus, from this simple example, it follows that the transfer of dye molecules from the dyebath phase to the fibre phase under the influence of the concentration gradient between the two phases (ie according to diffusion) will be twice as great when the lower of the two liquor ratios (ie 1:5) is employed.

Therefore, the promotional effect on direct dye uptake that is imparted by reduced liquor ratio can in part be explained in terms of the increased effective concentration of the dye in the dyebath and its effect upon diffusional dye transfer.

However, such diffusional transfer of dye from the dyebath phase to the fibre phase should, theoretically, cease when the dye concentration gradient between the two phases reaches zero, which will occur after ~50% transfer. This situation does not however occur in a commercial setting because diffusional dye transfer is not the sole driving force in dye adsorption, but, instead, the process of diffusion is augmented by dye-fibre substantivity (3).

Dye-fibre substantivity concerns the attraction between dye molecules and textile fibres and has both mechanical and physico-chemical origins (5). Although dye-fibre substantivity is conventionally interpreted in terms of the various intermolecular interactions (eg dispersion forces, ion-ion forces, etc.) that may operate between dyes and fibres, because it is virtually impossible to identify the extent to which one or other such interactions contribute towards dye-fibre attraction with any degree of certainty, coupled with the highly complex and little understood effects that polar water molecules have upon dye-fibre interactions, dye-fibre substantivity is a mostly unresolved phenomenon (5).

Despite the uncertainty that surrounds the precise origin and nature of dye-fibre substantivity, this highly important aspect of immersion dyeing can be readily and conveniently controlled during exhaust dyeing processes by adjusting both the physical conditions and/or physico-chemical aspects of dyeing (eg pH, dye-fibre interchange, etc.), which include, of relevance to the application of direct dyes to cellulosic fibres, both the selection of the liquor ratio used for dyeing as well as the addition of inorganic electrolyte to the dyebath. As such, the intrinsic tendency for dye molecules to transfer from the dyebath to the fibre that is imparted by dye diffusion (ie transfer under the influence of a dye concentration gradient) is augmented by dye-fibre substantivity. This is commonly achieved by using dyeing auxiliaries, which include added inorganic electrolyte in the case of direct dyes, as well as adjustment of the liquor ratio employed for dyeing.

In the latter context, because liquor ratio determines the amount of water that is used in a given dyeing process and, also, as water is of crucial importance in immersion dyeing processes, then water-dye and water-fibre interactions are principal determinant of dye-fibre substantivity; therefore, the solubility of a dye in a dyebath can be considered to be the principle factor which controls dye-fibre substantivity (3). According to this view, when the degree of dye-fibre substantivity that exists within an exhaust dyeing process is adjusted by manipulating the pH, temperature, etc. used for dyeing, such adjustments, in effect, regulate the aqueous solubility of the dye so as to expedite the tendency of the dye to favour the fibre phase rather than the aqueous dyebath phase (3). As direct dyes display characteristically high water solubility, then the control of direct dye-cellulosic fibre substantivity during dyeing has the principal aim of counteracting the intrinsic predisposition of the water-soluble dye to remain within the dyebath phase and, in so doing, shift the tendency of the dye in favour the substrate (3).

Despite the simplicity of this particular interpretation of the complex and little understood phenomenon of dye-fibre substantivity, a theoretical model was devised based upon this interpretation, which provided a practical explanation for the promotional effect imparted by added NaCl or Na_2SO_4 in the adsorption of direct dyes on cellulosic fibres. The model assumed that the aqueous solubility of a direct dye is the main contributor to dye-fibre substantivity and demonstrated that the solubility of the dye in the bulk dyebath phase determines the distribution of the dye between the fibre and dyebath phases (ie determines the extent of dye uptake) (3). The model was shown to be valid for dyeing carried out with the intention of achieving either non-equilibrium dye adsorption (ie commercial dyeing processes) or equilibrium dye adsorption and provided an explanation as to why the transfer of direct dye molecules from the aqueous phase to the fibre phase continues once the driving force provided by dye diffusion has ceased (3).

The model (3) revealed that the high aqueous solubility of direct dyes is responsible for not only their inherently low substantivity towards cellulosic fibres when applied in the absence of added inorganic electrolyte, but also, why added NaCl or Na_2SO_4 is so remarkably successful in promoting dye uptake. It was considered (3) that in the absence of added inorganic electrolyte, the dye prefers to remain in the aqueous dyebath phase rather than transfer to the fibre phase, because of the dye’s high aqueous solubility. Adding inorganic electrolyte to a direct dye dyebath encourages dye aggregation which reduces the solubility of the dye in the dyebath phase, so that the intrinsic preference of the previously highly soluble dye to favour the aqueous phase shifts towards the fibre phase and so dye uptake is promoted (3).

Such a model seems to be of interest from the viewpoint of the liquor ratio used in dyeing, since a reduction in liquor ratio will reduce the amount of water available for dye dissolution, which can be assumed will have implications in terms of dye solubility and, thus, the extent of dye uptake. Indeed, as will be demonstrated below, the theoretical model (3) proposed to explain the promotional effect imparted by added NaCl or Na_2SO_4 on the adsorption of direct dyes on cellulosic fibres can be employed to describe the promotional effect of reduced liquor ratio on direct dye uptake.

4.3 the use of two equations to describe the effect of liquor ratio on direct dye adsorption

Two approaches were used to derive an equation that interpreted the above model of direct dye adsorption on cellulosic fibres in terms of the effect of added inorganic electrolyte (3), namely one that sought to describe the distribution of the dye between the fibre and dyebath phases at the end of an immersion dyeing process and one that described the distribution of the dye between the two phases at any point throughout the immersion dyeing process. As described below, these two approaches were employed to derive equations to interpret the theoretical model of the manner by which liquor ratio influences direct dye uptake.

4.3.1 an equation that applies to dye uptake during immersion dyeing

According to the idea that dyeing takes place from within interstitial dye solution, as depicted by Figure 3, Eq 3 was derived to explain the promotional effect on direct dye uptake imparted by added NaCl or Na_2SO_4 (3), in which $[D]$ 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, $[D_{sol}]_f$ together with that present in the bulk dyebath dye solution in the dyebath phase, $[D_{sol}]_s$, and S is the substantivity coefficient.

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

The ratio $[D_{sol}]_f/[D_{sol}]_s$ describes the relative partition of the dye between the fibre phase and dyebath phase: the higher the value of this ratio then the greater is the partition 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 onto the substrate. As such, the ratio $[D_{sol}]_f/[D_{sol}]_s$ represents the substantivity of the direct dye towards the cellulosic fibre at a given stage within the immersion dyeing process. In this model, dye-fibre substantivity is expressed by the *substantivity coefficient*, *S*, which describes the ratio of the amount of dye in the interstitial dye solution, $[D_{sol}]_f$, to the amount of dye in the bulk dyebath dye solution,

$[D_{sol}]_s$. From Eq 3 it is evident that because of the term ($[D]$ - $[D_{sol}]_s/[D_{sol}]_s$), the degree of substantivity displayed by the dye towards the fibre, as represented by the substantivity coefficient, S, is determined by the concentration of dye in solution within the bulk dyebath, $[D_{sol}]_s$, 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 the extent of dye uptake.

Eq 3 therefore relates the degree of substantivity displayed by a direct dye towards a cellulosic fibre and the corresponding extent of dye uptake achieved, to the solubility of the dye; as such, Eq 3 provides an explanation for the nature of direct dye-cellulosic fibre substantivity based on the role of dye solubility.

As mentioned above, it was proposed (3) that the high aqueous solubility of direct dyes is responsible for both their inherent low substantivity towards cellulosic fibres when applied in the absence of added inorganic electrolyte, and, also, for the remarkable effectiveness of either NaCl or Na_2SO_4 in promoting dye; both of these aspects are predicted by Eq 3, as discussed below. When a direct dye is applied to a cellulosic fibre in the absence of added inorganic electrolyte, because of the dye's high aqueous solubility and its inherent preference for the aqueous dyebath, the dye will display a marked propensity to remain in solution within the bulk dyebath phase rather than transfer to the fibre phase. Under these conditions, Eq 3 shows that $[D_{sol}]_s$ will be high and, therefore, the term ($[D]$ - $[D_{sol}]_s/[D_{sol}]_s$) will be low, so that the substantivity coefficent, $[D_{sol}]_f/[D_{sol}]_s$, will also be low and dye uptake will not be favoured, as fits with practical observation. Thus, the substantivity coefficient, S (ie $[D_{sol}]_f/[D_{sol}]_s$) in Eq 3 describes the relative preference of the dye to favour either the fibre phase or the dyebath phase; the higher the value of this ratio then the greater is the preference 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 adsorption on the fibre.

When dyeing is carried out in the presence of added NaCl or Na_2SO_4, the aqueous solubility of the direct dye will be reduced because of electrolyte-induced aggregation. Thus, according to Eq 3, the concentration of dye in the solution within the bulk dyebath phase, $[D_{sol}]_s$, will be reduced so that the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$ will increase, which will result in the substantivity coefficient, $[D_{sol}]_f/[D_{sol}]_s$ also being increased and dye uptake will be promoted. As such, it was considered (3) that the effect of electrolyte-induced dye aggregation on direct dye uptake, as predicted by Eq 3, supported the view (2) that the application of direct dyes to cellulosic fibres in the presence of added NaCl or Na_2SO_4 represents the controlled precipitation of the dye from the aqueous dyebath onto the substrate.

4.3.1.1 the ability of the equation to predict changes in dye-fibre substantivity imparted by reduced liquor ratio

The relationship between liquor ratio and direct dye uptake can be explained using Eq 3 in terms of the combined effects which increased dye aggregation and reduced dye solubility have upon the solubility of the dye, in a manner analogous to that previously recounted (3) to explain the promotional effect of added inorganic electrolyte on direct dye uptake.

As the liquor ratio employed for dyeing increases, so $[D_{sol}]_s$ will increase because more water is available for a given amount of dye to dissolve; in contrast, $[D_{sol}]_s$ will decrease with decreasing liquor ratio because less water is available for a given amount of dye to dissolve. The last statement can be explained by reference to the marked propensity of direct dyes to aggregate in aqueous solution via coplanar association, and the fact that this particular attribute of direct dyes is encouraged in solutions of high dye concentration (2). When the liquor ratio of the dyebath is reduced, because the amount of water in which the direct dye molecules can dissolve is lowered, then the initial dye concentration in the dyebath will be increased correspondingly. Owing to the planar nature of direct dye anions and the likelihood of π-π interactions operating between aromatic centres within neighbouring dye molecules, which are responsible for the well-known tendency of direct dyes to aggregate in aqueous solution, the combined effects of reduced dyebath volume (ie amount of water available for dye dissolution) and greater initial dye concentration in the dyebath will encourage dye aggregation. Such aggregates will have lower aqueous solubility than their monomolecular direct dye counterparts owing to strong dye-dye interactions between neighbouring dye molecules and supressed ionisation of the dye molecules, that are promoted by hydrophobic interaction and the requirement of the water molecules that surround the dye solute molecules to minimise their interaction with the amphiphilic direct dye solutes and so reduce the disruption of the surrounding water structure by the dye molecules (2). Therefore, reducing the liquor ratio used for dyeing can be considered as a dilution factor because hydrophobic interaction results in reduced dye solubility and so the concentration of dye in the dyebath (ie $[D_{sol}]_s$) is lowered.

As discussed, in Eq 3, the substantivity coefficient, S (ie $[D_{sol}]_f/[D_{sol}]_s$) describes the relative preference of the dye towards the fibre and dyebath phases; the higher the value of this ratio then the greater is the preference 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 adsorption on the fibre. Since the magnitude of the substantivity coefficient is determined by the difference between the concentration of dye in solution in the bulk dyebath, $[D_{sol}]_s$, relative to the total amount of dye within the dyeing system, $[D]$, via the term ($[D] - [D_{sol}]_s/[D_{sol}]_s$), it follows that at high liquor ratios, $[D_{sol}]_s$ will be high and therefore, the term ($[D] - [D_{sol}]_s/[D_{sol}]_s$) will be low, so that the substantivity coefficent, $[D_{sol}]_f/[D_{sol}]_s$, will be correspondingly low and dye uptake will not be favoured, as observed in practice, owing to the direct dye's preference to remain within the aqueous dyebath phase. In contrast, at low liquor ratios, $[D_{sol}]_s$ will be reduced, so that the term ($[D] - [D_{sol}]_s/[D_{sol}]_s$) will increase, resulting in a high substantivity coefficient, $[D_{sol}]_f/[D_{sol}]_s$ so that dye uptake will be promoted, as also fits with practical observation.

Hence, the observed promotion of direct dye uptake onto cellulosic fibres imparted by lowering the liquor ratio employed for dyeing can be explained in terms of the combined effects which increased dye aggregation and reduced dye solubility have upon the substantivity coefficient, $[D_{sol}]_f/[D_{sol}]_s$. Lowering liquor ratio encourages dye aggregation which reduces the solubility of the dye in the dyebath phase, so that the intrinsic preference of the previously highly soluble direct dye to favour the aqueous phase shifts towards the fibre phase and so dye uptake is promoted. As discussed, this particular model was also advanced to describe the promotional effect of added inorganic electrolyte on the uptake of direct dyes on cotton and other cellulosic fibres (3).

By way of illustration, let us assume that 1 kg of cotton (moisture regain = 0.22 l kg^{-1}) is to be dyed to a 5% omf depth of shade using a pure sample of C.I. Direct Yellow 12, which has an aqueous solubility of 7.61 gl^{-1} that is reduced to 0.19 gl^{-1} and 0.069 gl^{-1} in the presence of 4 gl^{-1} and 10 gl^{-1} NaCl, respectively (12). If a 1:8 liquor ratio is employed for dyeing then because 22% of the dyebath volume (ie 1.76 l) will comprise interstitial dye solution within the fibre phase, $[D_{sol}]_f$, the volume of the dye solution in the bulk dyebath phase, $[D_{sol}]_s$, will be 6.24 l. As a 5% omf shade is to be applied (ie 50 g of dye for the 1 kg of cotton), the concentration of dye within the immersion dyeing system, $[D]$, will be 6.25 gl^{-1}, which is within the aqueous solubility limit of the dye (ie 7.61 gl^{-1}).

In the case of dyeing in the absence of added NaCl or Na_2SO_4, if it is assumed that no self-association of the dye molecules occurs, the amount of dye in the dye solution within the 6.24 l bulk dyebath phase, $[D_{sol}]_s$, will be 4.88 gl^{-1} (ie 6.24/8 * 6.25 gl^{-1}) which is again within the solubility of the dye in water (ie 7.61 gl^{-1}). Thus, from Eq 3, the substantivity coefficient, $S = [D_{sol}]_f / [D_{sol}]_s = 0.28$ (ie $([D] - [D_{sol}]_s/[D_{sol}]_s) = 0.28$) and, therefore, at a liquor ratio of 1:8, the partition of the dye between the dyebath and solution phases will favour the fibre phase, but only to a relatively small extent because of the dye's high solubility in water (in the absence of added inorganic electrolyte) and the preference of the dye for the bulk aqueous dyebath phase, $[D_{sol}]_s$. Thus, the innate tendency of the direct dye molecules to move from the dyebath phase to the fibre phase under the presence of a dye concentration gradient (ie according to diffusion) will receive a moderate boost from dye-fibre substantivity, although the overall level of substantivity displayed by the dye towards the cellulosic substrate will still be low, because of the dye's high solubility in the dyebath.

Let us now consider that the 5% omf dyeing of cotton using purified C.I. Direct Yellow 12 in the absence of added inorganic electrolyte are to be repeated but instead using liquor ratios of 1:4 and 1:1. Because the amount of water in the dyebath will decrease with decreasing liquor ratio, so the values of both $[D]$ and $[D_{sol}]_s$ will increase correspondingly, compared to that which prevailed when dyeing had been carried out using a 1:8 liquor ratio (ie $[D]$ = 6.25 gl^{-1} and $[D_{sol}]_s$ = 4.88 gl^{-1}). Thus, for the 1:4 and 1:1 liquor ratio dyebaths, the values of $[D]$ will be 12.5 gl^{-1} and 50 gl^{-1}, respectively and the corresponding values of $[D_{sol}]_s$ will be 9.75 gl^{-1} and 39.0 gl^{-1}, respectively. However, as the $[D_{sol}]_s$ values are greater than the solubility of the dye in the absence of added inorganic electrolyte (ie 7.61 gl^{-1}), the maximum concentration of dye in the bulk dyebath dye solution, $[D_{sol}]_s$ can only be 7.61 gl^{-1} and the remaining dye must therefore be present in the form of aggregates. Thus, from Eq 3, values for S = 0.64 and 5.57 are secured when dyeing is undertaken using liquor ratios of 1:4 and 1:1, respectively. In these cases, the tendency of the direct dye molecules to move from the dyebath to the fibre under the influence of a dye concentration gradient (ie according to diffusion) will receive a more meaningful boost from dye-fibre substantivity, because of the dye's reduced solubility in the dyebath.

Eq 3 therefore predicts that the partition of the dye between the dyebath and solution phases will favour the fibre phase for each of the three liquor ratios employed (ie 1:8, 1:4 and 1:1), but to an extent that increases with decreasing liquor ratio, as observed in practice. Hence, the dye displays lowest substantivity towards the cellulosic substrate at the highest liquor ratio (in this case 1:8) because of the dye's higher solubility in and preference for the bulk dyebath dye solution.

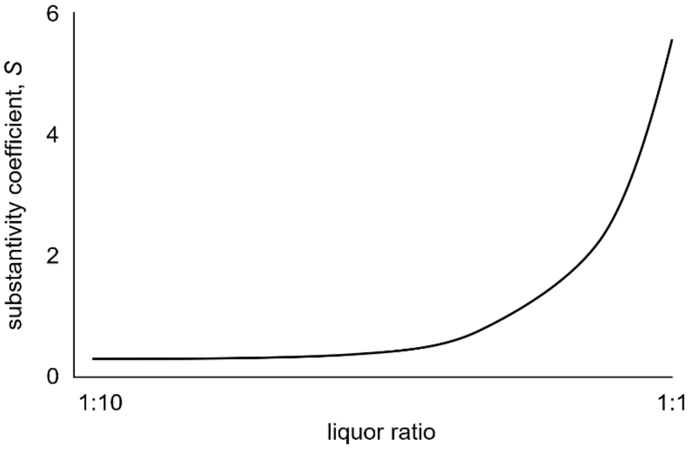


Figure 4 substantivity coefficient, S as a function of liquor ratio for C.I. Direct Yellow 12 in the absence of added inorganic NaCl using Eq 3

Lowering the liquor ratio to 1:4 or 1:1 reduces dye solubility and, therefore, dye-fibre substantivity increases because the preference of the dye for the bulk dyebath dye solution is lowered and transfer of the dye to the fibre phase is promoted. To illustrate this, Figure 4 shows a plot of substantivity coefficient, *S* as a function of liquor ratio over the range 1:10 to 1:1, calculated using Eq 3, employing the previously recounted solubility data for C.I. Direct Yellow 12. As the values of *S* displayed in Figure 4 reveal, Eq 3 predicts that dye uptake (expressed via *S*) increases with decreasing liquor ratio, as is observed in practice.

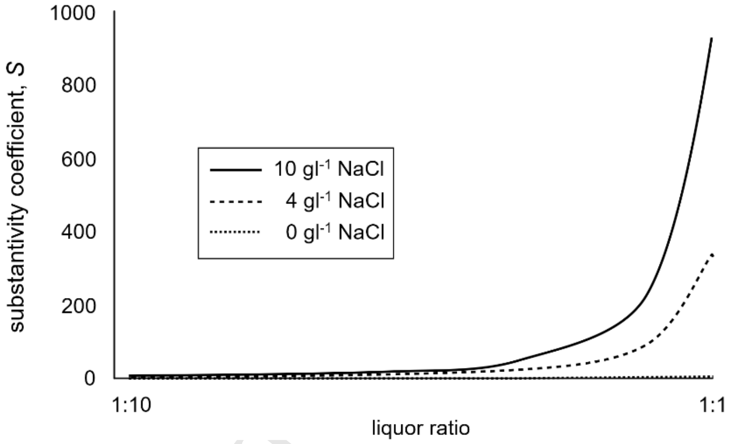


Figure 5 substantivity coefficient, *S* as a function of liquor ratio for C.I. Direct Yellow 12 in the presence and absence of added NaCl calculated using Eq 3

As mentioned, Eq 3 was originally derived to explain the promotional effect on direct dye uptake imparted by added inorganic electrolyte. As such, Eq 3 therefore describes the combined effects which liquor ratio and added NaCl or Na_2SO_4 impart to direct dye uptake. When the above calculations were repeated but, in this case, assuming that C.I. Direct Yellow 12 was applied over the range of 1:10 to 1:1 liquor ratios in both the absence and presence of 4 gl^{-1} and 10 gl^{-1} NaCl, again using the dye solubility data of reference (12), the data displayed in Figure 5 were secured. As Figure 5 reveals, Eq 3 predicts that dye uptake, expressed via the substantivity coefficient, *S*, increases with both decreasing liquor ratio and increasing amount of added inorganic electrolyte, as fits with practical observation, because reducing the liquor ratio used for dyeing and adding either Na_2SO_4 or NaCl to a direct dyebath each result in reduced dye solubility, as described by Eq 3.

Eq 3 therefore accounts for the well-known fact that liquor ratio and added inorganic electrolyte have a combinatorial effect on dye uptake, which is reflected in commercial immersion dyeing processes used to apply direct dyes to cellulosic fibres, insofar as, in order to ensure that uniform dyeings of the desired depth of shade are obtained within a given dyeing time, the level of dye-fibre substantivity is manipulated by using a particular amount of added inorganic electrolyte in combination with a particular liquor ratio (and at a given dyeing temperature). In this way, the relative contributions of liquor ratio and added NaCl or Na_2SO_4 to the overall level of dye-fibre substantivity are regulated. Thus, if the liquor ratio selected for dyeing is changed, then a corresponding change in the amount of added electrolyte is made (and visa versa).

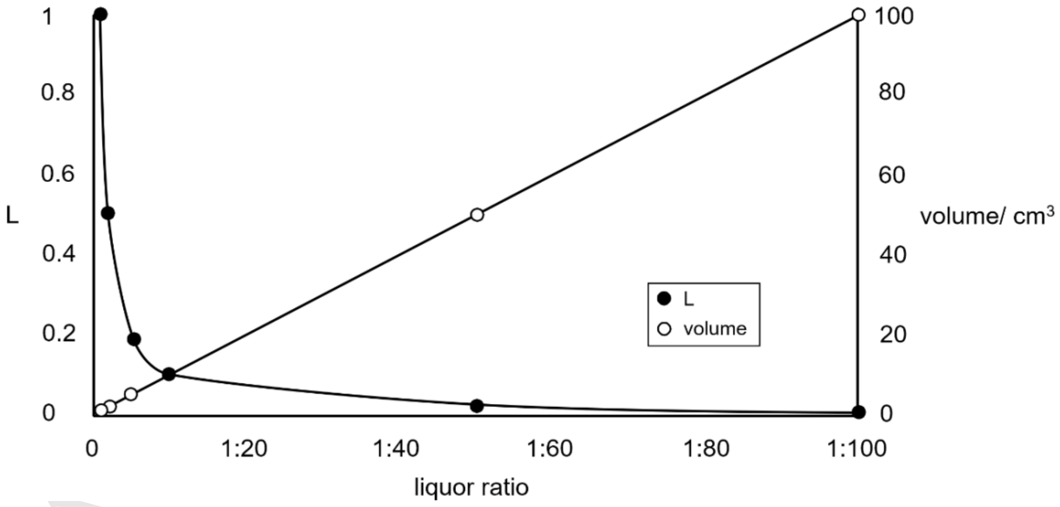


Figure 6 variation of fractional liquor ratio, *L* and dyebath volume as a function of liquor ratio over the range 1:1 to 1:100

The relationship between the promotional effect of reduced liquor ratio on direct dye uptake expressed via dye solubility, as described in Eq 3, can be further articulated, quantitatively, by modifying Eq 3. Because liquor ratio is a fraction, as exemplified by 1/5, 1/10, etc. then values of the *fractional liquor ratio*, *L*, increase with decreasing liquor ratio. For example, values of *L* (units of L will be mass (of fibre) per unit volume (of dyebath), such as kg l^{-1}) increase 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 through to 0.2 for a liquor ratio of 1:5, as illustrated by the exponential curve shown in Figure 6 for liquor ratios varying from 1:1 to 1:100.

$$\mathrm{L} = \frac{\mathrm{m}}{\mathrm{v}} \qquad 4$$

$$[D] = [D_{sol}]_f m + [D_{sol}]_s v \qquad 5$$

As fractional liquor ratio is given by Eq 4 in which *m* is the mass of fibre and *v* the volume of dyebath used in dyeing, these two parameters can be used to define the total amount of dye, [D], present within the immersion dyeing system, via Eq 5, since the amount of dye that will be present in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$ depends on the amount of fibre present in the dyeing system via its mass, *m*, and the amount of dye that will be present in the bulk dyebath dye solution in the dyebath phase, $[D_{sol}]_s$, depends on the amount of dyebath present in the dyeing system, via its volume, *v.*

Substituting from Eq 5 into Eq 3 provides Eq 6.

$$S = \frac{[D_{sol}]_f m}{[D_{sol}]_s v} = \left(\frac{[D] - [D_{sol}]_s\, v}{[D_{sol}]_s v}\right) \qquad 6$$

From Eq 4 it follows that Eq 7 holds, then substituting for *v* in Eq 6 gives Eq 8.

$$\mathrm{v} = \frac{\mathrm{m}}{\mathrm{L}} \qquad 7$$

$$S = \frac{[D_{sol}]_f}{\frac{[D_{sol}]_s}{L}} = \left(\frac{[D] - \frac{[D_{sol}]_s}{L}}{\frac{[D_{sol}]_s}{L}} \right) \qquad 8$$

Owing to the term (*[D_{sol}]$_s$/L*) in Eq 8, liquor ratio, via *L*, impacts directly on the amount of dye in solution in the bulk dyebath phase, *[D_{sol}]$_s$, r*ather than on the amount of dye in the interstitial solution in the fibre, *[D_{sol}]$_f$*. This is because values of *[D_{sol}]$_s$* will decrease markedly with decreasing liquor ratio since values of *L* increase with decreasing liquor ratio (eg value of *L* @ a given liquor ratio: 0.01 @ 1:100; 0.02 @ 1:50; 0.1 @ 1:10; 0.2 @ 1:5; 1 @ 1:1) and, therefore, values of *[D_{sol}]$_f$* will decrease accordingly.

Indeed, the proposal represented by Eq 8, that *[D_{sol}]$_s$* increases with increasing liquor ratio, fits with practical observation insofar as, whilst the numerical value of *L* decreases, exponentially, with increasing liquor ratio (Figure 6), the amount of water in the dyebath increases linearly with increasing liquor ratio, as shown in Figure 6 for liquor ratios varying from 1:1 to 1:100.

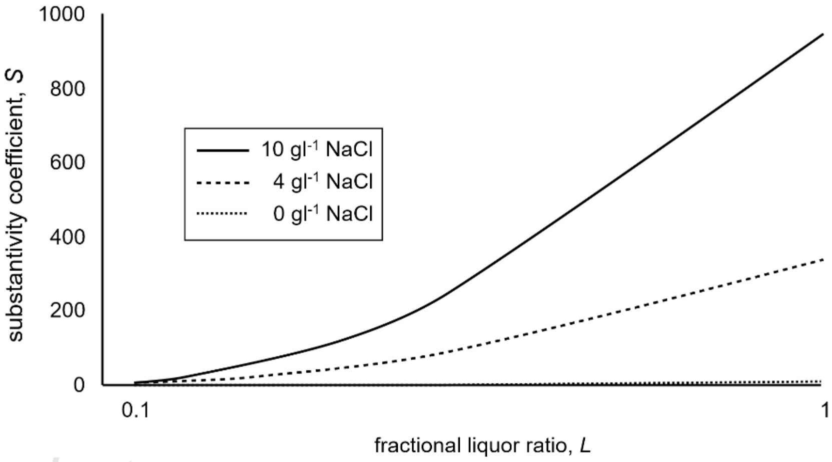


Figure 7 substantivity coefficient, *S* as a function of fractional liquor ratio, *L* for C.I. Direct Yellow 12 in the presence and absence of added NaCl calculated using Eq 8

To illustrate this, Figure 7 shows a plot of *S* as a function of fractional liquor ratio, *L*, assuming that C.I. Direct Yellow 12 was applied over the range *L* = 0.1 to 1 (corresponding to a liquor ratio range of 1:10 to 1:1) in both the absence and presence of 4 gl^{-1} and 10 gl^{-1} NaCl, again using the dye solubility data of reference (12).

In Eq 8, the concentration of dye in both the dyebath phase $[D_{sol}]_s$ and fibre phase, $[D_{sol}]_f$, as well as the total amount of dye within the immersion dyeing system, $[D]$, are measured in mass per unit volume (eg $g\ l^{-1}$), whilst the units of fractional liquor, L, ratio are mass per unit volume, such as $kg\ l^{-1}$. Because of the term ($[D] - [D_{sol}]_s/L\ /\ [D_{sol}]_s/L$), the substantivity coefficient S therefore has dimensions of mass per unit volume (eg gl^{-1}). This situation parallels that described previously (3) in the case of a theoretical model that invoked the concept of interstitial water in dyeing and which described the effect of added inorganic electrolyte on direct dye uptake. Thus, the earlier argument (3) can be used to support the view that dimensions of mass of dye per volume of dyebath (eg $g\ l^{-1}$) seem reasonable for the substantivity coefficient, S, in Eq 8.

In effect, both Eq 3 and Eq 8 suggest that the observed increased uptake of direct dyes that accompanies a reduction in the liquor ratio employed for dyeing is a process of controlled precipitation of the dye within the fibre, since the solubility of the dye in the dyebath is reduced and the partition of the dye shifts in favour of the fibre phase, as was proposed (3) in the case of the effect of added inorganic electrolyte on direct dye uptake.

4.3.1.2 the influence of liquor ratio in the context of an interstitial dyeing mechanism

It is possible to explain the promotional effect of reduced liquor ratio on direct dye uptake in terms of the interstitial dyeing mechanism which had previously been employed to explain the promotional effect of added inorganic electrolyte on the uptake of direct dyes on cellulosic fibres (3).

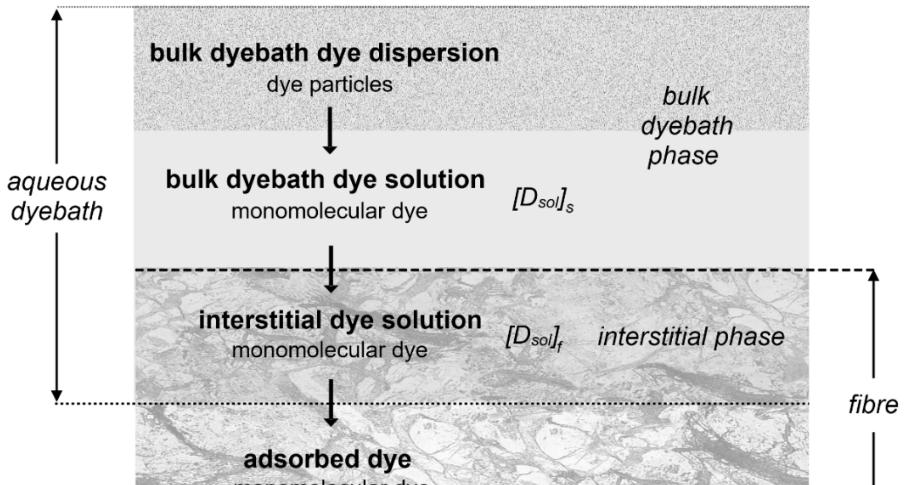


Figure 8 representation of direct dyeing mechanism (3)

With reference to Figure 8, when direct dyes are applied to cellulosic fibres in the absence of added inorganic electrolyte, at the start of dyeing, the aqueous dyebath, which comprises both the interstitial phase and the bulk dyebath phase, will contain monomolecularly dissolved dye ions. However, owing to the well-known inclination of direct dye molecules to aggregate in solution at low temperature, even in the absence of added electrolyte (13, 14), the bulk dyebath phase will also contain a proportion of the dye in the form of aggregates that will comprise dye molecules of lower solubility than non-aggregated direct dye molecules which will be present in the surrounding aqueous dye solution in the dyebath. As the dye aggregates will likely tend to coalesce and form dye particles, these can also be expected to be present within the dyebath in the form of a dispersion. Thus, the aqueous dyebath at the start of dyeing will contain a heterogeneous assembly of direct dye molecules that are present in different physical states namely highly soluble, ionised (monomolecular) dye molecules, low solubility dye aggregates that comprise reduced solubility dye molecules as well as low solubility dye particles that contain clusters of dye aggregates. The dyebath will therefore contain a proportion of the dye in the form of dissolved dye molecules (ions) present within a dye solution, dye aggregates that will be present within a suspension, as well as dye particles that will constitute a bulk dyebath dye dispersion phase. Such a situation can be expected to be favoured when low liquor ratios are used for dyeing, as it is well known that dye aggregation in solution is promoted by an increase in dye concentration, as will occur when liquor ratio is reduced (ie when the amount of water available for dye dissolution is reduced).

As dyeing proceeds and dyeing temperature increases, the proportion of dye particles within the dyebath can be presumed to fall, since dye aggregation is reduced by increasing temperature.

Thus, at the temperatures generally used to apply direct dyes to cellulosic fibres (~80-95°C) the dye will likely be present mostly in monomolecular form and the ensuing dye ions will display high aqueous solubility in both the interstitial and bulk dyebath phases. Nonetheless, at low liquor ratios, even at the high temperatures utilised for dyeing, the proportion of the dye in the dyebath that is present as monomolecular, high solubility, dye anions (ie $[D_{sol}]_s$) will be much lower than might be expected to prevail at higher liquor ratios.

As dissolved dye molecules that reside within the interstitial dye solution interact with the substrate and become adsorbed (Figure 8), dissolved dye molecules present in the bulk dyebath dye solution transfer to the interstitial dye solution, from which further dye molecules can be adsorbed by the fibre. Dye molecules are then released from the dye particles within the bulk dyebath dye dispersion, which dissolve in, and replenish the bulk dyebath dye solution, from which dissolved dye ions can transfer to the interstitial dye solution, so that further dye adsorption is enabled. This process of dye dissolution from the bulk dyebath dye dispersion to the bulk dyebath dye solution → dye molecule transfer from the bulk dyebath dye solution to the interstitial dye solution → dye adsorption from the interstitial dye solution (as depicted by Figure 8) continues until either all of the dye has been adsorbed or the fibre is saturated with dye.

Thus, this model, which utilises the concept of interstitial water, is analogous to that proposed to account for the promotional effect imparted to direct dye uptake imparted by adding NaCl of Na_2SO_4 to a direct dye dyebath. Both models therefore predict that adding inorganic electrolyte and reducing the liquor ratio used for dyeing have the same outcome, namely, that dye uptake is promoted because dye aggregation in the dyebath is encouraged, as a result of which, the solubility of the dye in the dyebath is reduced, so that, according to both Eq 3 and Eq 8, the substantivity coefficent, $[D_{sol}]_f/[D_{sol}]_s$, will increase and dye uptake will be favoured, as is observed in practice.

Such a finding has important consequences, as it implies that reducing the liquor ratio used for dyeing and adding inorganic electrolyte to a direct dye dyebath have a combinatorial effect upon dye uptake, in that both actions exert similar influences upon dye-fibre substantivity which indeed fits with practical observations. Thus, the supposition implicit in both Eq 3 and Eq 8, that direct dye uptake is related to the solubility of the dye in the dyebath, concurs with the previously mentioned practical dyebath behaviour that the adjustment of dye-fibre substantivity by manipulating physical factors and physico-chemical aspects, has one aim, namely, to regulate dye solubility.

However, both Eq 3 and Eq 8 only relate the solubility of the direct dye to its likely distribution between the interstitial dye solution in the fibre phase and the bulk dye solution in the dyebath phase, which does not take into account the contribution of other dyebath variables that contribute to dye-fibre substantivity (eg temperature, dyebath-fibre interchange rate, etc.). The values of the substantivity coefficient, S (ie $[D_{sol}]_f$ / $[D_{sol}]_s$) obtained using Eq 3 and Eq 8 are therefore indicative only, insofar as, a high value of S implies that reduced dye solubility in the dyebath promotes dye uptake whilst a low value of S suggests that high dye solubility in the dyebath demotes dye uptake.

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

Assuming 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 1, as was previously demonstrated in the case of added inorganic electrolyte (3). This particular approach will be shown below to be of practical use, as it enables previously published data concerning the effect of reduced liquor ratio on the (final) uptake of direct dyes on cellulosic materials, to be analysed from the viewpoint of establishing the manner by which reduced liquor ratio in the presence of a constant amount of added inorganic electrolyte promotes dye uptake.

Eq 9 was derived to explain the promotional effect on final direct dye uptake imparted by added NaCl or Na_2SO_4 (3), in which $[D]$ is the total amount of dye within the immersion dyeing system, $[D]_f$

the amount of dye present in the fibre phase relative to the amount of fibre and $[D]_s$ the amount of dye in solution (ie the dyebath) relative to the amount of solution, and S is the substantivity coefficient of the direct dye.

$$S = \frac{[D]_f}{[D]_s} = \left(\frac{[D] - [D]_s}{[D]_s}\right) \qquad 9$$

The ratio $[D]_f/[D]_s$ in Eq 9 describes the relative partition of the dye between the fibre and dyebath phases: the higher the value of this ratio then the greater is the partition of the dye in favour of the fibre phase (ie $[D]_f > [D]_s$) and the greater is the extent of dye uptake onto the substrate. As such, the ratio $[D]_f/[D]_s$ 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. Owing to the term ($[D]$ - $[D_{sol}]_s/[D_{sol}]_s$), the magnitude of S depends upon 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 in dye concentration, the higher is dye-fibre substantivity, and, therefore, the greater the extent of dye uptake.

In deriving Eq 9, it was assumed (3) that dyeing takes place from within interstitial dye solution located in the fibre and, therefore, 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, $[D]$, are expressed in mass per unit volume (eg g l^{-1}), so that according to the term ($[D]$ - $[D]_s/[D]_s$), the substantivity coefficient S has dimensions of mass per unit volume (eg gl^{-1}). This situation parallels that described in the case of the model of direct dye adsorption that invoked the concept of interstitial water in dyeing (section 5.1) and the same argument can therefore be used to propose that dimensions of mass of dye per volume of dyebath (eg g l^{-1}) seem reasonable for substantivity coefficient, S, in Eq 9. Indeed, the similarity between Eq 9 and Eq 5 is clearly apparent.

Eq 9 therefore provides a model in which the degree of substantivity displayed by the direct dye towards the cellulosic fibre, as expressed in terms of the substantivity coefficient, S, is linked to the final extent of dye uptake (ie $[D]_f/[D]_s$) via the solubility of the dye in the dyebath, $[D]_s$.

According to the proposal that the solubility of the direct dye will be reduced because of reduced liquor ratio, it follows that $[D]_s$ will be lowered, so that the term ($[D]$ - $[D]_s/[D]_s$) will increase and, therefore, the dye concentration gradient (ie $[D]_f/[D]_s$) will increase. Thus, according to Eq 9, the partition of the dye between the fibre and solution phases, will increase with decreasing liquor ratio because the amount of dye in solution, $[D]_s$, is lowered and, therefore, the amount of dye in the fibre phase, $[D]_f$, increases accordingly. Hence, Eq 9 predicts, as does Eq 3, that it is the amount of dye in solution, which is determined by the solubility of the dye in the aqueous dye solution in the dyebath phase, that governs the amount of dye that is adsorbed by the substrate at the end of dyeing.

The effect of liquor ratio on the final distribution of dye between the fibre and dyebath phases achieved at the end of the immersion dyeing can be further expressed by modifying Eq 9.

As liquor ratio is a fraction, expressed by Eq 4, the total amount of dye, $[D]$, present within the fibre, f and dyebath, s phases can be described using Eq 10.

$$[D] = [D]_f m + [D]_s v \qquad 10$$

Substituting into Eq 9 gives Eq 11.

$$S = \frac{[D]_f m}{[D]_s v} = \left(\frac{[D] - [D]_s v}{[D]_s v}\right) \qquad 11$$

From Eq 7, substituting for v in Eq 11 provides Eq 12.

$$S = \frac{[D]_f}{\frac{[D]_s}{L}} = \left(\frac{[D] - \frac{[D]_s}{L}}{\frac{[D]_s}{L}} \right) \qquad 12$$

Eq 12 therefore defines the relationship between the distribution of the dye between the fibre, $[D]_f$, and solution, $[D]_s$, phases, expressed in terms of the substantivity coefficient, S, and fractional liquor ratio, L. In terms of the partition of the dye between the fibre and dyebath phases, as described by the ratio $[D]_f/([D]_s/L)$, owing to the term ($[D]_s/L$) it is apparent that liquor ratio impacts directly on the amount of dye in solution rather than on the amount of dye in the fibre insofar as, values of $[D]_s$ will decrease with decreasing liquor ratio and, therefore, values of $[D]_f$ will increase accordingly. For example, because values of L increase with decreasing liquor ratio (eg $L = 0.02$ at a liquor ratio of 1:50, $L = 0.1$ at a 1:10 liquor ratio and $L = 0.2$ at a liquor ratio of 1:5) then a value of $[D]_s$ of say, 10, secured using a 1:5 liquor ratio can be expected to increase to 100 if a liquor ratio of 1:10 was employed. From this simple example, it follows that it is the effect of liquor ratio on the amount of dye in solution that will influence the final partition of the dye between the fibre and solution phases.

This is further reflected in terms of the marked influence which the solubility of the dye in the dyebath has upon the substantivity coefficient, S, of the dye, because of the term ($[D]-[D]_s/L$ / $[D]_s/L$) in Eq 12, according to which, the substantivity of the dye (ie 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, $[D]_f$. The predictions inherent in Eq 12 that $[D]_s$ increases with increasing liquor ratio, accords with practical observation, as depicted in the relationships described in Figure 6, between the numerical value of L and the amount of water in the dyebath as a function of liquor ratio.

The similarity between Eq 12 and Eq 8 is evident and, therefore, the arguments previously recounted in section 5.1.1 can be used to show that the observed promotion of direct dye uptake onto cellulosic fibres imparted by lowering the liquor ratio employed for dyeing can be explained in terms of the combined effects which increased dye aggregation and reduced dye solubility have upon the substantivity coefficient, S, of the dye.

In Eq 8, whereas the concentration of dye at the end of the dyeing system in both the dyebath phase $[D]_s$ and fibre phase, $[D]_f$, as well as the total amount of dye within the immersion dyeing system, $[D]$, are measured in mass per unit volume (eg g l^{-1}), the units of fractional liquor, L, ratio are mass per unit volume, such as kg l^{-1}. Hence, because of the term ($[D] - [D]_s/L \,/\, [D]_s/L$) in Eq 12, the substantivity coefficient S has dimensions of mass per unit volume (eg gl^{-1}). This situation parallels that described above (section 5.1.1) in the case of the theoretical model that invoked the concept of interstitial water in dyeing.

As the driving force for dyeing from a thermodynamic perspective is usually expressed in terms of some derivative of Eq 1, it follows that the thermodynamic affinity of a dye will also vary as a function of liquor ratio; this will be discussed in a subsequent part of this paper.

4.3.3 comparison of the two equations

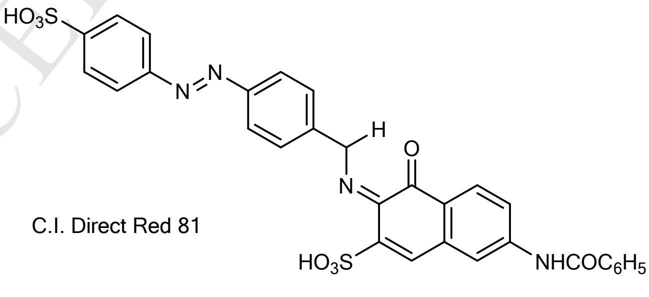
Both Eq 3 and Eq 9 provide explanations for the promotional effect imparted by reduced liquor ratio on direct dye adsorption. Despite the similarity of the two equations, they differ in terms of both the particular stages of the dyeing process to which they apply and the nature of the data that is required for their solution. Eq 3 describes the motivational force that augments dye diffusion in promoting the transfer of the dye molecules from the dyebath phase to the fibre phase during dyeing. Whilst Eq 3 requires information about the aqueous solubility of the dye in both the interstitial dye solution and the bulk dyebath solution, collecting this data presents challenges, as the aqueous solubility of direct dyes is difficult to determine accurately owing to practical difficulties (2). Eq 9 offers an experimentally more amenable alternative, because the final distribution of the dye between the dyebath and fibre phases at the end of an immersion dyeing process requires knowledge of the experimentally accessible amounts of dye present in the solid fibre and the exhausted dyebath at the end of dyeing. Both models suggest that direct dyeing should be achievable in the complete absence of added inorganic electrolyte using low liquor ratios.

In a similar manner Eq 8 and Eq 13 are both able to explain the promotional effect of reduced liquor ratio on the immersion direct dyeing system. Whilst the two equations are similar, for reasons analogous to those recounted above, the two models differ in terms of the particular stages of the exhaust dyeing process to which they apply and the nature of the data that is required for their solution. Once again, both models suggest that direct dyeing should be achievable in the complete absence of added inorganic electrolyte using low liquor ratios.

However, the relationship between dye uptake and liquor ratio, *L*, expressed via the substantivity ratio, *S* in Eq 8 or Eq 13, is qualitative only, since the correlation between dye uptake and liquor ratio is not straightforward, quantitatively, as discussed below.

5 analysis of published data

As a means of interrogating the above theoretical considerations, an analysis is presented below of published experimental results that had been obtained in an especially detailed investigation (15) of the effects of liquor ratio on direct dye adsorption.



C.I. Direct Red 81

In this particular study (15), Bird *et a*l applied purified C.I. Direct Red 81 to a union of cotton and wool fabrics employing five liquor ratios (1:20, 1:40; 1:60; 1:80 and 1:100) and varying amounts of added Na_2SO_4, ranging from 10% omf to 50% omf, so as to maintain a constant concentration (5 gl$^-$

^{1}) of the electrolyte whilst liquor ratio was varied; dyeing was undertaken at four different temperatures namely, 40°C, 60°C, 80°C and 98°C.

Figure 9 reveals that dye uptake, *[D]$_f$*, decreased with increasing liquor ratio, findings that agree with those of other authors [eg (7, 16, 17)]. It is also evident that dye uptake decreased with increasing liquor ratio for each of the four dyeing temperatures used, the plots of *[D]$_f$* versus liquor ratio being displaced to higher values of dye uptake as dyeing temperature increased. Based on the notion that liquor ratio is a dilution factor that determines the amount of water available in the dyebath for dissolution (or dispersion) of the dye molecules, the promotional effect which decreasing liquor ratio has upon dye uptake, as depicted by the plots shown in Figure 9, can initially be attributed to a corresponding increase in the concentration of the dye in the dyebath and the effect which this has upon the transfer of dye molecules from the dyebath phase to the fibre phase under the influence of the concentration gradient between the two phases (ie according to diffusion).

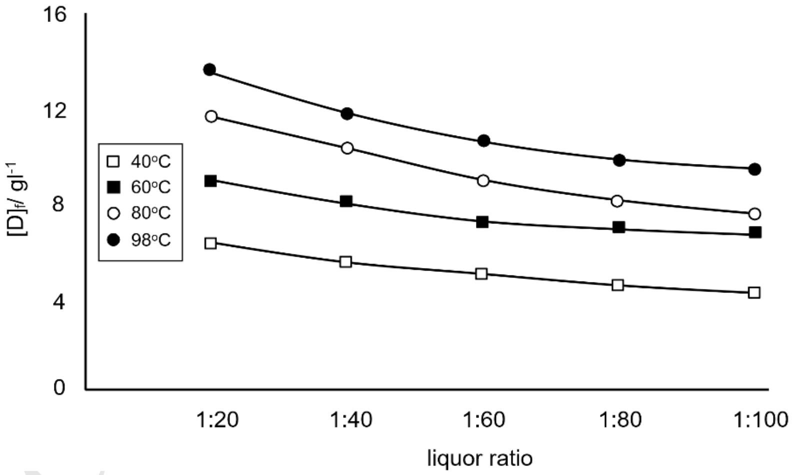


Figure 9 Effect of liquor ratio on uptake of purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1} Na_2SO_4; plotted using data from (15)

In this context, as Bird *et al* (15) applied a 3% omf depth of shade, then in going from a 1:100 to a 1:20 liquor ratio, the concentration of C.I. Direct Red 81 in the dyebath at the start of dyeing would increase by a factor of five, based on liquor volume (ie 0.3 g l^{-1} @ 1:100; 0.375 g l^{-1} @ 1:80; 0.5 gl^{-1} @ 1:60; 0.75 g l^{-1} @ 1:40; 1.5 g l^{-1} @ 1:20).

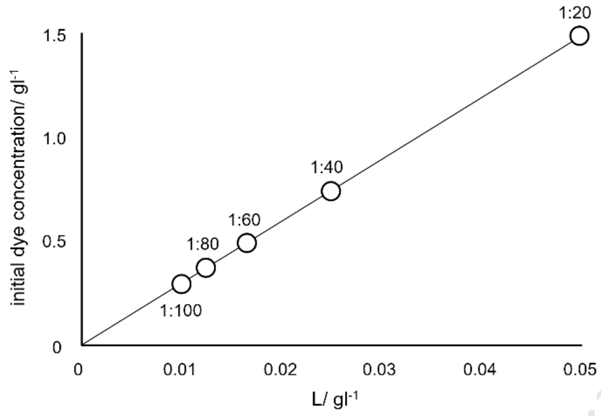


Figure 10 initial dye concentration as a function of fractional liquor ratio

When these values of initial dye concentration are plotted as a function of fractional liquor ratio, an essentially linear relationship is obtained (Figure 10; the various liquor ratios that correspond to the values of *L* are displayed in the figure). Thus, if increased diffusional dye transfer that resulted from increased initial dye concentration in the dyebath was a major contributor to the promotional effect of reduced liquor ratio on dye uptake depicted in Figure 9, the extent of this contribution might be expected to reflect the linear relationship observed between initial dye concentration and liquor ratio shown in Figure 10.

However, the curvilinear relationship observed for the dye uptake as a function of initial dye concentration (Figure 11; the corresponding liquor ratios are displayed on the graph) does not correlate with the linear variation of initial dye concentration as a function of liquor ratio (Figure 10). Therefore, it seems reasonable to suggest that the increase in the concentration of the direct dye in the dyebath that accompanied a reduction in the liquor ratio used for dyeing made only a small contribution to the observed promotional effect imparted by decreased liquor ratio on dye uptake (Figure 9).

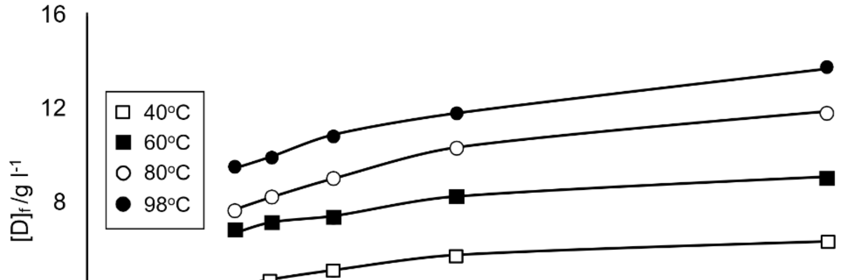


Figure 11 Effect of initial dyebath concentration on uptake of purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1} Na_2SO_4; plotted using data from (15)

Hence, the increase in dye uptake that accompanied a decrease in liquor ratio (Figure 9) cannot simply be attributed to a corresponding increase in the transfer of dye molecules from the dyebath to the fibre under the influence of the concentration gradient between the two phases (ie according to diffusion).

The results obtained by Bird *et al* (15) can be interpreted using Eq 12 since, as mentioned, this equation describes the partition of the dye between the dyebath, *s* and fibre, *f*, phases in terms of the substantivity coefficient, *S*, secured at the end of the immersion dyeing process.

Figure 12 shows a plot of $[D]_f$ as a function of $[D]_s/L$ for purified C.I. Direct Red 81, plotted using the data of Bird *et al* (15), at each of the four dyeing temperatures used (40, 60, 80 and 98^{o}C) and for each of the liquor ratios employed (the liquor ratios are indicated on the figure). From Eq 12, it follows that the values shown in Figure 12 are those of the substantivity coefficient, *S*, achieved at each liquor ratio, for each of the four temperatures used. Figure 12 reveals that for each dyeing temperature, the values of *S* decreased as the liquor ratio increased from 1:20 to 1:100. The overall reduction in substantivity coefficient secured at the four temperatures and five sets of liquor ratio can be described by the dotted line shown in Figure 12.

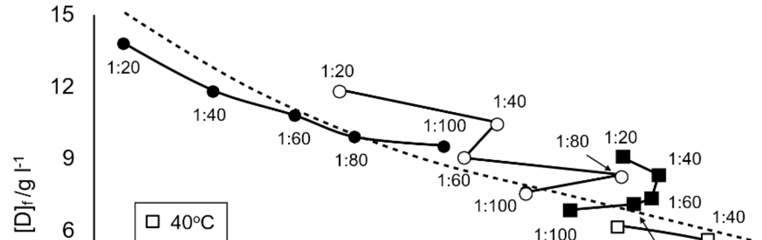


Figure 12 Effect of liquor ratio and temperature on partition of purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1} Na_2SO_4; plotted using data from (15)

As such, the dotted line describes the overall effect of change in liquor ratio (ie from 1:20 to 1:100) on the partition of the dye between the fibre and dyebath phases over the temperature range studied (ie 40-98°C). The scales of the two axes reveal that values of $[D]_s/L$ were greater than those of $[D]_f$ and, from the negative slope of the dotted line, it is evident that the difference between the values of $[D]_f$ and $[D]_s/L$ decreased with increasing dyeing temperature.

Thus, the data displayed in Figure 12 show that the contribution of $[D]_s/L$ was greater than that of $[D]_f$ in terms of the observed reduction in partition coefficient imparted by a decrease in liquor ratio, although the contribution of $[D]_s/L$ diminished as dyeing temperature increased. These results imply that it was the amount of dye present in the dyebath, $[D]_s$, which determined the amount of dye adsorbed by the fibre, $[D]_f$, and, thereby, the partition of the dye between the dyebath and fibre phases.

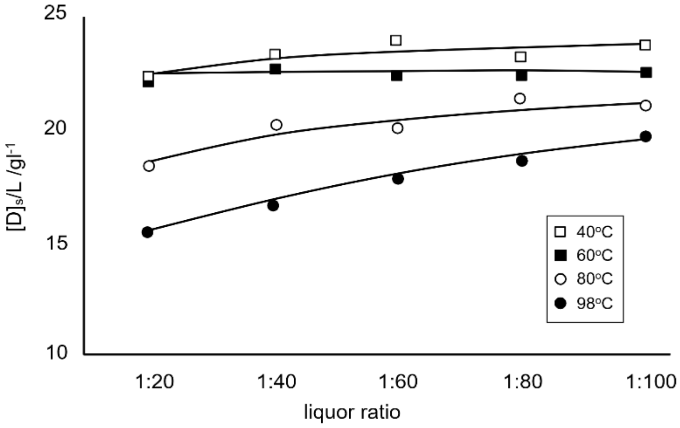


Figure 13 Effect of liquor ratio on dye concentration in solution; purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1} Na_2SO_4; plotted using data from (15)

Support for this proposal accrues from the findings in Figure 13 that the concentration of dye in solution (ie the dyebath), $[D]_s/L$, increased with increasing liquor ratio. From the foregoing discussion, this can be attributed to there being more water available for the given amount of dye to dissolve. The observation that the contribution of $[D]_s/L$ diminished as dyeing temperature increased is reflected in the plots shown in Figure 13 which show that values of $[D]_s/L$ decreased with increasing dyeing temperature (ie followed the order: 40°C > 60°C > 80°C > 98°C), for each of the five liquor ratios used. However, this finding contrasts to that observed for the effect of dyeing temperature on values of $[D]_f$ (Figure 9), which were found to increase with increasing dyeing temperature, (ie followed the order: 98°C > 80°C > 60°C > 40°C) for each of the five liquor ratios used. This can be explained by assuming that as dyeing temperature increases, more dye will dissolve in solution and, therefore, more dye will be available for dye uptake. Also, both the rate and extent of dye diffusion within the fibre can be expected to increase with increasing dyeing temperature. Thus, since $[D]_s/L$ increases with increasing dyeing temperature then so too will $[D]_f$.

Since Bird *et al* (15) employed added electrolyte (Na_2SO_4) to apply the disulphonated C.I. Direct Red 81, the effect of liquor ratio on the concentration of electrolyte in the dyebath at the start of dyeing warrants discussion. In early work concerned with the classification of the dyeing behaviour of direct dyes, Lemin *et al* (7) observed considerable divergence between the dyeing performance of a range of commercial direct dyes at two different liquor ratios (1:5 and 1:60) and concluded that the most important contribution to this observed effect was the electrolyte content of the commercial dyes used. Commercial dyes contain various additives (anti-dusting agents, buffers, antifoams, etc.), including neutral electrolytes such as Na_2SO_4 and/or NaCl that are incorporated into the commercial dye powder, liquid, etc (5) as part of the process that is used to obtain commercial dye products (powders, liquids, etc.) of the desired tinctorial strength. The nature and amount of the particular formulation additive used, varies, according to aspects such as the type of dye, intended dyeing method, etc. In the case of direct dyes, as neutral electrolyte is likely to be present in commercial dye samples, such additive will be present in the dyebath during dyeing. Lemin *et al* determined that the electrolyte present in commercial dye samples would impart a much greater promotion of dye exhaustion when low liquor ratios were used for dyeing than when large liquor ratios were employed for dyeing (7). Since the liquor ratio that Bird *et al* used varied from 1:100 to 1:20 then so too would the concentration of additive electrolyte in the dyebath. To avoid this, Bird *et al* (15) used a purified (ie additive-free) sample of C.I. Direct Red 81 in their study.

According to the SDC classification system for direct dyes (18), some direct dyes which can be controlled by electrolyte addition alone at higher liquor ratios may require additional temperature control when applied using lower liquor ratios. Furthermore, when the amount of electrolyte utilised in dyeing is expressed as % omf rather than mass per volume, such as gl^{-1}, then a given amount of added electrolyte will impart a greater influence on dye exhaustion as liquor ratio decreases. To address these issues, the amounts of added Na_2SO_4 used by Bird *et al* (15) (ie 10%, 20%, 30%, 40% and 50% omf) were such that a constant concentration of added electrolyte (5 gl^{-1}) was present in the dyebath, despite the fact that the liquor ratio varied from 1:20, 1:40, 1:60, 1:80 and 1:100. Thus, in the data collected by Bird *et al* (59), even though the effective dye concentration in the dyebath at the start of dyeing increased by a factor of five based on liquor volume (as the amount of dye used was calculated on the basis of % omf), in going from a 1:100 to a 1:20 liquor ratio, the effective concentration of added electrolyte in the dyebath was the same irrespective of liquor ratio. Hence, the observed increase in dye uptake that accompanied a decrease in liquor ratio (Figure 9) cannot be attributed to an increase in electrolyte concentration in the dyebath and, therefore, the promotional effect of reduced liquor ratio on dye uptake can be assumed to relate to a characteristic of the dye alone.

To expand upon this proposal, brief excursions into dye aggregation in solution, fibre swelling and dye diffusion in the fibre seem appropriate.

As mentioned, characteristically, direct dyes are long, planar molecules solubilised by sulfonic acid/ sulfonate groups, as exemplified by the three dyes used in this work, and exhibit a pronounced tendency to aggregate in aqueous solution. Such aggregation, which is exacerbated by added inorganic electrolyte, generally decreases with increasing temperature and decreasing dye concentration. In the context of the results presented in Figures 12 and 13, at a 1:20 liquor ratio, C.I. Direct Red 81 will be more aggregated than at a 1:100 liquor ratio and, therefore, because aggregation reduces with decreasing dye concentration, the solubility of the dye in the dyebath will increase with increasing liquor ratio (ie values of $[D]_s/L$ will increase with increasing liquor ratio in accordance with Eq 12, as previously discussed). This relationship was indeed secured by Bird *et al* (15) and is shown in Figures 12 and 13, insofar as values of $[D]_s/L$ increased as liquor ratio increased over the range 1:20 to 1:100, for each of the four dyeing temperatures used. As aggregation generally decreases with increasing temperature (5), it follows that at 40^{o}C, dye aggregation in the dyebath will be greater than when dyeing had been carried out at 98^{o}C and, therefore, $[D]_s/L$ will increase as dyeing temperature increases. Thus, at higher dyeing temperatures, the amount of dye in the dyebath available for adsorption by the fibre will be higher than at lower temperatures.

In addition, at higher temperatures, it is likely that fibre swelling will also be greater than at lower dyeing temperatures, as also will be both the rate and extent of dye diffusion within the fibre (5). As dye aggregation in the dyebath will decrease with increasing dyeing temperature then the amount of dye in the dyebath will be higher, enabling more dye to diffuse within the more swollen fibre. As a corollary, it follows that as dyeing temperature increased from 40^{o}C to 98^{o}C (Figures 12 and 13), the amount of C.I. Direct Red 81 adsorbed by the substrate $[D]_f$ increased but the amount of dye remaining in the dyebath, $[D]_s/L$, decreased, as demonstrated by the results displayed in Figures 12 and 13. Indeed, as mentioned, the dotted line in Figure 12 depicts the overall effect of temperature on the partition coefficient of the dye. The slope of the dotted line reveals that at a high dyeing temperature (98^{o}C) values of $[D]_f$ and $[D]_s/L$ are similar whereas at a low temperature (40^{o}C) values of $[D]_f$ are much lower than those of $[D]_s/L$. Thus, $[D]_s$ is the dominant factor in determining the extent of uptake by the fibre and, therefore, the partition of the dye between the dyebath and fibre phases.

In this context, Figure 14 shows the variation of substantivity coefficient, *S*, calculated using Eq 12, as a function of liquor ratio achieved for purified C.I. Direct Red 81 on CV. It is apparent that the slope of the curved lines obtained at each dyeing temperature increased with increasing temperature, which can be attributed to a corresponding increase in fibre swelling and dye diffusion within the fibre, as well as a reduction of dye aggregation within the dyebath.

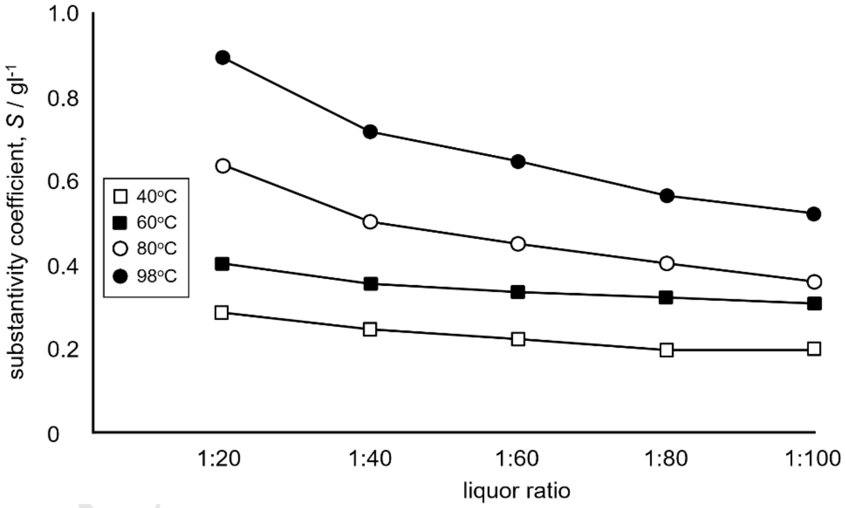


Figure 14 Effect of liquor ratio on substantivity coefficient of purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1} Na_2SO_4; plotted using data from (15)

As the latter aspect may well be the major contributing factor, it seems appropriate to consider the possible influence of dye aggregation in the dyebath on dye uptake. For this, the plots of $[D]_f$ as a function of $[D]_s/L$ shown in Figure 12 will be examined. From Eq 12 it is evident that the four curves displayed in Figure 12 describe the corresponding substantivity coefficient, *S* values (ie $S = [D]_f / [D]_s/L$) obtained when dyeing had been carried out the four different dyeing temperatures. It is apparent that the *S* values obtained when dyeing had been carried out at 98°C decrease, almost linearly with increasing liquor ratio. In the case of dyeing at 80°C, the *S* values take the form of an 'S' shape; however, when dyeing had been undertaken at 60°C and, especially, at 40°C, v-shaped curves were secured. These findings can be attributed to the well-known fact that increasing temperature reduces the extent of dye aggregation in solution (5) insofar as the marked dye aggregation that is likely to occur at 40°C and 60°C will be much less pronounced at the higher dyeing temperatures employed (ie 80°C and especially 98°C). Indeed, the linearity of the *S* values obtained at 98°C (Figure 12) suggests that the direct dye is little aggregated in solution whilst the v-shaped curve obtained at 40°C is indicative of extensive aggregation. In such a situation, it follows that the slope of the curved lines shown in Figure 12 increase with increasing dyeing temperature because of a corresponding reduction in the extent of aggregation in solution.

In this context, as discussed above, according to the model of direct dye uptake described by Eq 12, the inherently low substantivity displayed by the dyes towards cellulosic fibres in the absence of added electrolyte is attributable to the dye's marked preference for the aqueous dyebath phase, which stems from the dye's high aqueous solubility. Reducing the liquor ratio used for dyeing encourages dye aggregation which reduces the solubility of the dye in the dyebath phase, so that the intrinsic preference of the previously highly soluble dye to favour the aqueous phase shifts towards the fibre phase and so dye uptake is promoted. Thus, it follows that the substantivity of the dye, as expressed by the substantivity coefficient, should decrease with increasing liquor ratio, at each of the four dyeing temperatures employed, as indeed was found to be the case (Figure 15).

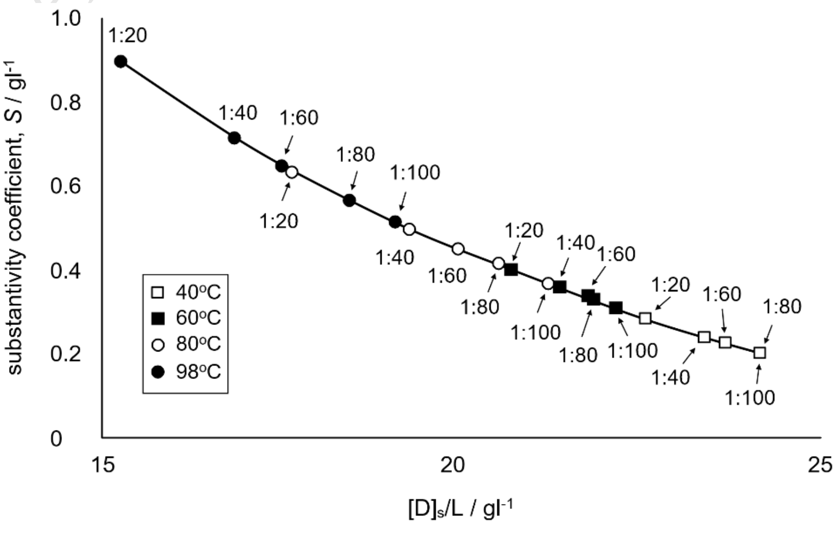


Figure 15 variation of substantivity coefficient as a function of $[D]_s/L$; purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1} Na_2SO_4; plotted using data from (15)

Interestingly, the variation of S as a function of $[D]_s/L$ depicted in Figure 15 bears a close resemblance to the variation of $[D]_f$ as a function of $[D]_s/L$ shown in Figure 12, insofar as both plots have negative slopes and the arrangement of the individual data points relating to the particular liquor ratio used, as shown by the coincidence of variation of the substantivity coefficient, S, and $[D]_f$, as a function of $[D]_s/L$ in Figure 16. Indeed, the curvilinear plots secured for the variation of both S and $[D]_f$ as a function of $[D]_s/L$ depicted in Figure 16 are not too distant cousins, which implies that Eq 12 (ie $S = ([D] – [D]_s/L/ [D]_s/L)$ appears to provide a reasonable fit to the experimentally observed variation of $[D]_f$ as a function of liquor ratio. In turn, this suggests that the assumptions inherent in Eq 12 namely that reducing the liquor ratio used for dyeing reduces the solubility of the dye in the bulk dyebath phase, because of increased dye aggregation, so that the inherent preference of the dye to favour the aqueous phase shifts towards the fibre phase.

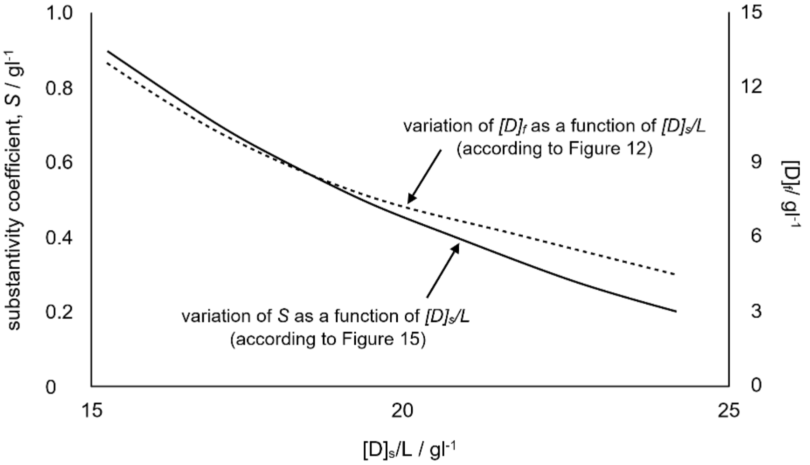


Figure 16 coincidence of variation of substantivity coefficient, S, and of $[D]_f$, as a function of $[D]_s/L$

6 conclusions

According to the concept that the immersion application of direct dyes to cellulosic fibres takes place from within interstitial dye solution located in the wetted, swollen fibre, a theoretical model has been devised to relate the partition of the dye between the fibre and dyebath phases to the amount of dye in solution within the dyebath.

The model is based on the premise that the solubility of the dye in the dyebath is the primary determinant of direct dye-cellulosic fibre substantivity and, therefore, of the tendency of the dye to favour either the fibre phase or dyebath phase. As such, the intrinsic high aqueous solubility of direct dyes is responsible for the inherently low substantivity displayed by the dyes towards cellulosic fibre. In addition, the dye's high solubility is also the reason why lowering the liquor ratio used for dyeing promotes dye uptake so effectively. It is proposed that by lowering the liquor ratio used for dyeing, the solubility of the dye in the dyebath is reduced and, as a consequence, dye-fibre substantivity increases and so dye uptake is thereby promoted.

Two equations were derived to interpret the theoretical model of direct dye. Each equation invoked the concept of interstitial water in dyeing, but 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.

In order to interrogate the proposed model of dyeing, an analysis of published work on the influence of liquor ratio on the uptake of purified C.I. Direct Red 81 in the presence of a constant concentration of added Na_2SO_4, using one of the mathematical derivatives of the theoretical model, confirmed that lowering liquor ratio reduces the solubility of the dye in the dyebath phase as a result of increased dye aggregation, so that the inherent preference of the dye to favour the aqueous phase shifts towards the fibre phase.

As the same theoretical model accounts for the promotion of direct dye uptake imparted by the addition of inorganic electrolyte to direct dye dyebaths, it can be concluded that reduced liquor ratio and added inorganic electrolyte exert a combinatorial promotional effect on direct dye uptake.

Each of the two mathematical representations of the theoretical model suggest that the dyeing of cellulosic fibres using direct dyes should be achievable in the complete absence of added inorganic electrolyte by adopting low liquor ratios. This is the subject of the next part of the paper insofar as a series of dyeings were carried out on cotton fabric using three direct dyes, in which various liquor ratios were employed in both the absence and presence of added NaCl and the results were interpreted using the proposed theoretical models of the manner by which both reduced liquor ratio and added inorganic electrolyte enhance direct dye uptake on cellulosic substrates.

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