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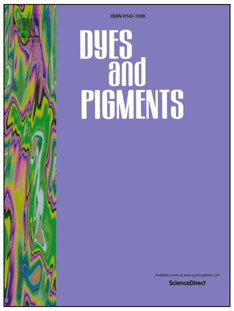

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The role of auxiliaries in the immersion dyeing of textile fibres Part 2: analysis of conventional models that describe the manner by which inorganic electrolytes promote direct dye uptake on cellulosic fibres

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Abstract

An analysis is provided of the various concepts and theories that have been proposed to account for the manner by which added NaCl or Na_2SO_4 promotes the uptake of direct dyes on cellulosic fibres. Although conventional approaches to describe the mechanism by which direct dye adsorption occurs entail the use of complex mathematical interpretations of isothermal equilibrium dye adsorption data, such interpretations are unable to satisfactorily explain not only why direct dyes display inherently low uptake on cellulosic fibres in the absence of added inorganic electrolyte but also why added inorganic electrolyte is so effective in promoting dye uptake.

Highlights

- inorganic electrolyte is widely used in cellulosic fibre dyeing
- various theories have been proposed to explain the role of electrolyte
- such theories provide only approximate explanations

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

abbreviations

CLY: lyocell; CV: viscose; PES polyethylene terephthalate; omf: on mass of fibre

1 Introduction

This paper concerns the application of dyes to textile fibres from aqueous dyebaths using immersion dyeing processes and the role of some of the common auxiliaries that are employed in such dyeing processes. Although dyeing auxiliaries have enjoyed widespread usage for many centuries and a substantial number of different types of auxiliary are nowadays available, the precise mode of action of many auxiliaries has not been fully resolved. This paper seeks to examine the mechanism of action of common auxiliaries that are used in the application of dyes to textile fibres from aqueous dyebaths using immersion processing

From a global perspective, considerable amounts of dyeing auxiliaries are consumed annually; indeed, the consumption of dyebath auxiliaries is considered to be 60-70% of that of dyes (1). Whilst detailed statistics relating to global dye usage are unavailable in the public domain, an estimate can be made (2) based on published figures for world fibre production and assuming that an average of 2% on mass of fibre (omf) dye is used for textile coloration. According to this particular approach, as world textile fibre production in 2015 was 90.6 x 10^6 T (3), of which cotton & man-made cellulosic fibres accounted for ~31% (28.1 x 10^6 T) and PES fibres ~58.5% (53.1 x 10^6 T), with wool, silk and other natural fibres making up only a very small proportion (~1.4%; 1.2 x 10^6 T) and other man-made and synthetic fibres comprising ~9.1% (~8.2 x 10^6 T), then, of the estimated global dye consumption of ~1.8 x 10^6 T in 2015, some 1.1–1.3 x 10^6 T of auxiliary would have been consumed in textile dyeing.

In the first part of the paper (4) the different types of auxiliary and the nature of the assistance they impart to immersion dyeing processes were discussed, together with both environmental and financial aspects associated with their use, as well as a discussion of the relationship between liquor ratio and the use of auxiliaries in immersion dyeing. In view of the enduring global popularity of cotton and other cellulosic fibres such as lyocell (CLY) and viscose (CV) [usage in 2015 being ~28.1 x 10^6 T (4)], this part of the paper will consider the role of the most fundamentally important dyeing auxiliary utilised in the dyeing of cotton and other cellulosic fibres with direct dyes, namely inorganic electrolyte, in the form of either sodium chloride or sodium sulfate.

By way of brief introduction, added inorganic electrolyte is routinely added to direct dye dyebaths in order to promote both the rate and extent of uptake on cellulosic fibres; indeed, added NaCl or Na_2SO_4 has been an essential constituent of all exhaust direct dyeing processes for cellulosic fibres for well over a century. The use of inorganic electrolyte in direct dyeing has attracted considerable research interest and many theories have been proposed to explain its effect upon dye uptake promotion. However, none of these theories adequately describes the promotional effect of inorganic electrolyte upon direct dye uptake; furthermore, none of the proposed theories can be interpreted in terms of the currently accepted physico-chemical mechanism by which direct dyes are adsorbed onto cellulosic fibres.

The primary objective of the work described in this part of the paper was to clarify the precise manner by which added inorganic electrolyte influences direct dye uptake on cellulosic substrates. As such, this part of the paper presents a critical analysis of published research studies relating to the influence of added inorganic electrolyte on the uptake of direct dyes on cellulosic substrates.

Subsequent parts of the paper will discuss how the findings from this analysis can be used to develop a theoretical model which explains the promotional effect imparted by added inorganic electrolyte on the uptake of direct dyes on cellulosic fibres. It will also be subsequently demonstrated that the same theoretical model can be employed to describe the promotional effect on direct dye uptake imparted by a reduction in the liquor ratio utilised for dyeing. In a later part of the paper, it will be shown that when experimental results obtained for the application of direct dyes to cotton are interpreted using these two theoretical models, it is possible to explain why cotton (and other cellulosic fibres) can be dyed using direct dyes employing an immersion process in the complete absence of added electrolyte at low liquor ratio.

2. added electrolyte in the dyeing of cellulosic fibres

Five classes of dye can be used to dye cotton and other cellulosic fibres namely reactive dyes, sulphur dyes, vat dyes, azoic colorants and, of relevance to this part of the paper, direct dyes. As a corollary of the continued growth in the popularity of reactive dyes over the past 60 or so years since their commercial introduction, global consumption of the other four classes of dye has declined and direct dyes nowadays account for around 11% of global dye consumption for cellulosic fibres (Figure 1). Of the previously mentioned estimated global dye consumption of 1.81 x 10^6 T in 2015, the proportion that was used to dye cellulosic fibres would have been ~560,000 T, with ~10-12% of this amount, equivalent to some 56,000-67,000 T, being direct dyes.

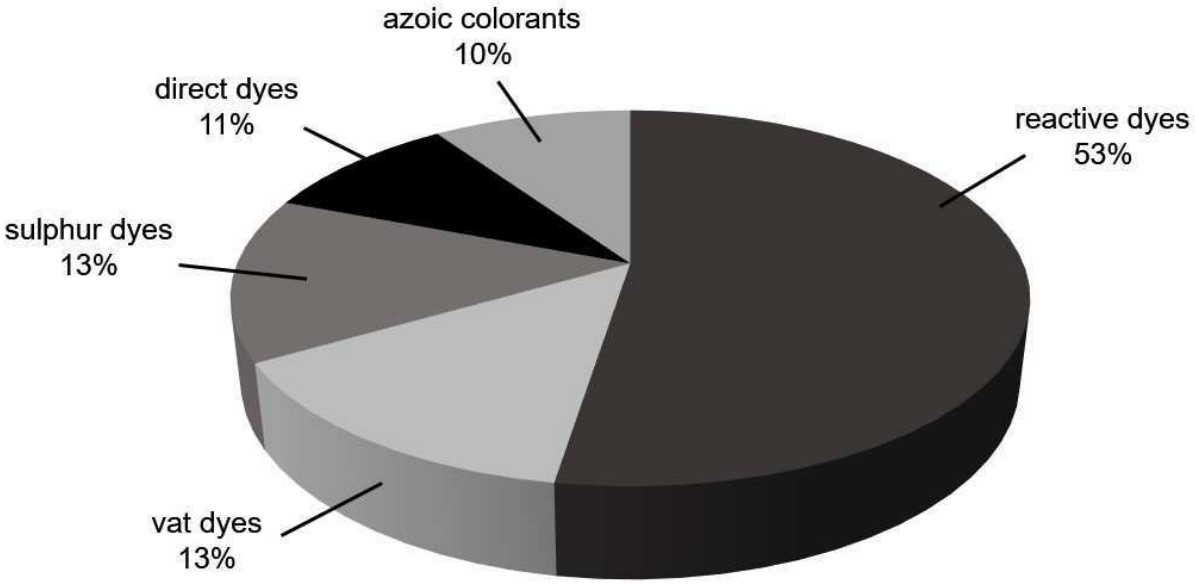


Figure 1 estimated consumption of dyes for cellulosic fibres

Despite the seemingly unstoppable growth in the popularity of reactive dyes over the past six or so decades and the fact that direct dyes account for only ~10-12% of the dyes that are used on cellulosic fibres, the amount of direct dye employed globally in dyeing, is, nonetheless, substantial. The reasons for the commercial resilience of direct dyes include the inherent simplicity of the immersion dyeing process as well as the ability of the dyes to furnish typically low cost, bright shades in pale/medium depths of moderate-good light fastness. Although dyeings on cellulosic fibres typically display only poor-moderate wet fastness (eg towards washing, water, etc.), an aftertreatment of the dyeing with a cationic fixing agent can secure much improved levels of wet fastness.

The above mentioned five classes of dye vary not only in terms of both their aesthetic and technical characteristics on cellulosic fibres (eg brightness, shade range, fastness, etc.) but also in terms of the conditions that are used for their exhaust application (eg temperature, pH, etc.). Nevertheless, the five dye classes share one inherent feature, namely that the immersion application of selected azoic coupling components, leuco vat anions and sulphur anions, as well as reactive dyes and direct dyes to cellulosic fibres, routinely entails the addition of added electrolyte (NaCl or Na_2SO_4) to the dyebath in order to promote dye uptake; in the case of reactive dyes, the added electrolyte also promotes dye fixation. The amount of electrolyte employed in dyeing varies not only between different classes of anionic dye, as exemplified by the data shown in Table 1 for direct dyes and reactive dyes, but also between different members of the same dye class.

Table 1 Typical electrolyte usage for direct and reactive dyes on cotton (5)

depth of shade	amount of dye/ %omf	amount of electrolyte / g l^{-1}	
		direct dyes	reactive dyes
pastel/light	<1.5	2.5-7.5	30-50
medium	1.0-2.5	7.5-12.5	70-80
dark	>2.5	12.5-20.0	80-100

The latter aspect is illustrated by the findings that different amounts of added NaCl, ranging from 0 to 30% omf, were required to achieve the same level (50%) of exhaustion of different direct dyes on CV (6); furthermore, the uptake of various, purified direct dyes onto both cotton and CV in the presence of 5 gl^{-1} NaCl demonstrated similar, considerable variation (6).

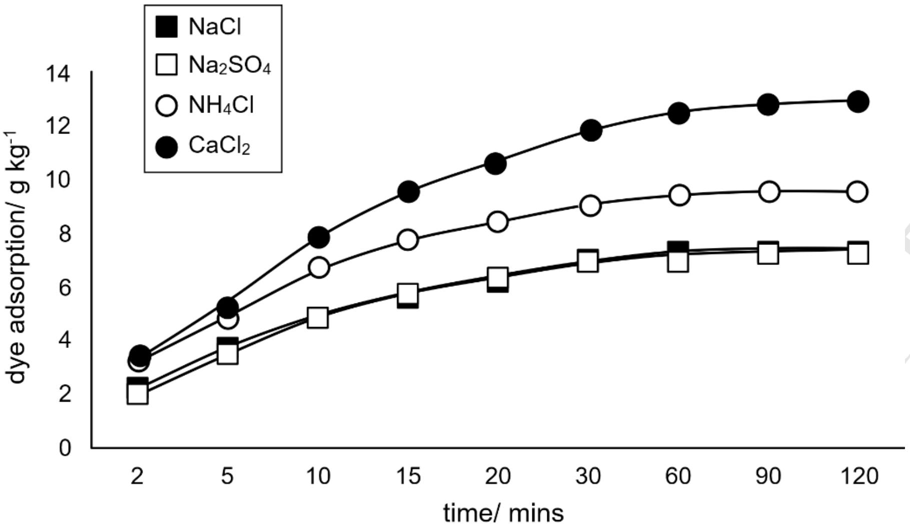


Figure 2 Effect of added electrolyte on adsorption of purified C.I. Direct Blue 1 on CV sheet; 0.05 gl^{-1} dye; 0.0855M electrolyte; 98°C; plotted using data from (7)

Three types of inorganic electrolyte are commonly used in cellulosic fibre dyeing namely anhydrous (aka calcined) sodium sulfate, Na_2SO_4, sodium sulfate decahydrate (Glauber's salt) Na_2SO_4 x 10 H_2O and sodium chloride (1 kg of NaCl ≡ 1.22 kg Na_2SO_4 or 2.78 kg Na_2SO_4 x 10 H_2O). Despite the widespread popularity of NaCl and Na_2SO_4 in the immersion application of direct dyes to cellulosic fibres, the use of other inorganic electrolytes has received attention from the viewpoint of the promotion of dye uptake [eg (7-12)]. In essence, whilst similar levels of dye adsorption are generally achieved using equivalent amounts of univalent cations, divalent cations impart greater levels of adsorption [eg (7, 8)], as illustrated by the data shown in Figure 2 and the finding (7) that upto concentrations of 0.1M electrolyte, the promotion of uptake of purified C.I. Direct Blue 1 (**I**) on CV sheet imparted by the added electrolyte, followed the order:

$$BaCl_2 > CaCl_2 > ZnSO_4 > MgCl_2 > NH_4Cl > NaCl > KH_2PO_4 > Na_2HPO_4$$

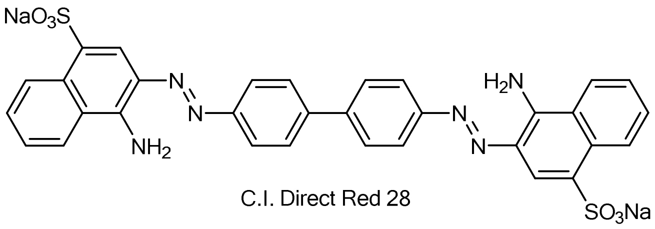
An estimate can be made of the scale of NaCl and Na_2SO_4 usage in cellulosic fibre dyeing, as well as the magnitude of the sizeable environmental and economic burdens posed by treatment of the ensuing saline dyeing wastewater. Although precise figures for the amount of water used globally for dyeing are unavailable, an indicative estimate can be obtained by assuming an average liquor ratio for immersion dyeing of 1:8 (2). In this context, as world production of cotton & man-made cellulosic fibres in 2015 was 28.1 x 10^6 T (3), of which 10-12% was dyed using direct dyes, if dyeing had been carried out using immersion processes employing a 1:8 liquor ratio then between 22.5 x 10^6 T and 26.9 x 10^6 T of water would have been consumed in dyeing using direct dyes. In terms of current commercial practice, as the exhaust application of direct dyes to cellulosic fibres is carried out in the presence of between 5 gl^{-1} and 20 gl^{-1} added NaCl or Na_2SO_4, then this would mean that between ~112,000 and 540,000 T of added inorganic electrolyte would have been used in the exhaust dyeing of cellulosic fibres with direct dyes in 2015. However, this sizeable usage of added inorganic electrolyte consumed in direct dyeing is spectacularly eclipsed by that encountered in the dyeing of cellulosic fibres with reactive dyes, since, by some margin, the majority of global cellulosic fibre production is dyed using this dye class (Figure 1) and upto 100 gl^{-1} added NaCl or Na_2SO_4 can be used for exhaust dyeing (Table 1). In this case, assuming that all reactive dyeing had been carried out using immersion application at a 1:8 liquor ratio in the presence of 100 gl^{-1} added salt then 120 x 10^6 T of water and 12 x 10^6 T of added electrolyte would have been consumed in 2015. However, as mentioned, three other classes of dye can be used to dye cotton and other cellulosic fibres, namely sulphur dyes, vat dyes and azoic colorants. Since the immersion application of each of these three dye classes to cellulosic fibres also commonly entails the addition of added NaCl or Na_2SO_4 to the dyebath to promote dye uptake, then this electrolyte usage will increase the already unacceptably high levels of inorganic electrolyte that are consumed in the immersion application of direct dyes and reactive dyes.

Despite the overly simple approach adopted in the above calculations, it is apparent that from a global perspective, the immersion dyeing of cellulosic fibres using direct dyes (and reactive dyes) nevertheless involves the use of outrageously high levels of added electrolyte; the magnitude of the ensuing environmental challenges that treatment of the resulting saline wastewater present is also evident. As discussed in the first part of the paper (4), added electrolyte in cellulosic fibre dyeing poses both major economic and environmental problems not only because of the large amounts of electrolyte that are routinely employed in dyeing but also because of the significant environmental hazard that both NaCl and Na_2SO_4 present in terms of the treatment and disposal of dyeing wastewater. Although a wide range of possible methods have been examined for treating dyeing effluent (4) no single method has yet been identified that can deal with the complex and varied nature of dyeing wastewater. In this context, the impact of dyeing auxiliaries on the effectiveness of wastewater decolourisation and re-use has attracted attention [eg (13-15)].

From this very brief discussion of the magnitude of inorganic electrolyte usage in cellulosic fibre dyeing and the consequent environmental problems posed by the ensuing saline wastewater, it seems reasonable to proffer that if it was possible to apply direct dyes (as well as other types of anionic dyes and dye precursors) to cellulosic fibres in the absence of added electrolyte, considerable environmental and economic advantages might be achieved.

3 why is inorganic electrolyte used in the dyeing of cellulosic fibres with direct dyes?

The use of added electrolyte to promote the uptake of direct dyes onto cotton and other cellulosic fibres dates from the latter part of the C19th. Briefly, in 1883, the young chemist Paul Böttiger synthesised a novel, red azo dye from tetrazotised benzidine coupled to two moles of sodium 1-naphthylamine-4-sulfonate, and observed that the dye could be applied to cotton in the presence of added electrolyte. In 1884, Böttiger obtained a patent for the dye and, in the following year, AGFA began selling the colorant under the trade name *Congo Red* (16-18). As such, Böttiger had invented the first azo dye that could be applied *directly* to cotton without the need for a mordant and the dye that he had invented, *Congo Red* (C.I. Direct Red 28), became the first member of the dye class known in the Colour Index as *direct dyes* (2, 19).



C.I. Direct Red 28

The marked promotional effect which added electrolyte has upon the uptake of direct dyes on cellulosic fibres, as first observed by Böttiger in the case of C.I. Direct Red 28 on cotton, has been the subject of considerable investigation and debate, and is illustrated by the results shown in Figure 3 which reveal that added electrolyte, in this case calcined sodium sulfate, increased both the rate and extent of uptake of the six direct dyes studied. This characteristic response of direct dyes to added electrolyte is one aspect of the well-known structure-dependent dyeing behaviour of direct dyes on cellulosic fibres that is embodied in the *ABC* classification system for direct dyes devised by the Society of Dyers and Colourists (SDC) (20, 21), which considers the migrating ability, response to temperature, as well as influence of liquor ratio and behaviour towards added electrolyte of direct dyes on cellulosic fibres. Owing to differences in the dyeing behaviour of individual direct dyes on cellulosic substrates, dye makers commonly specify optimum application conditions (temperature, electrolyte concentration, etc.) for their particular range(s) of direct dyes.

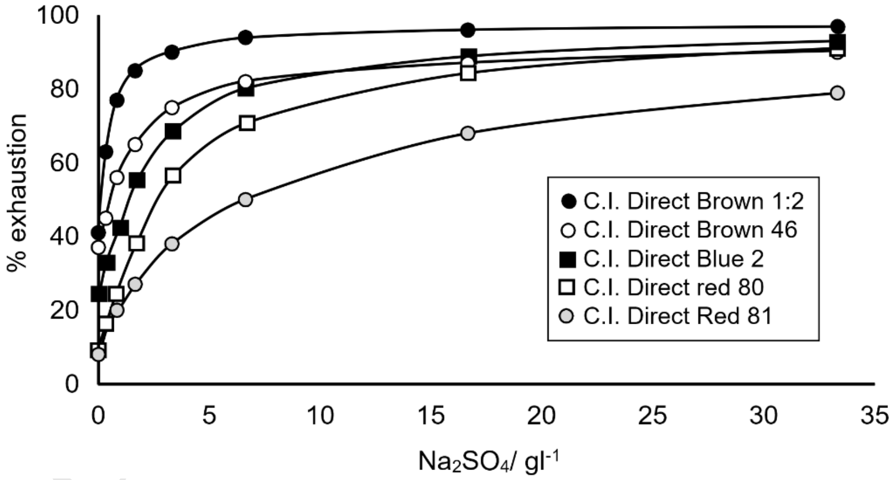
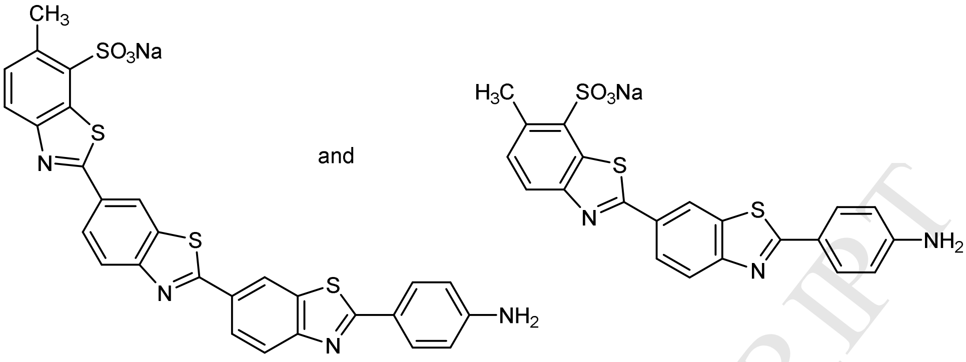
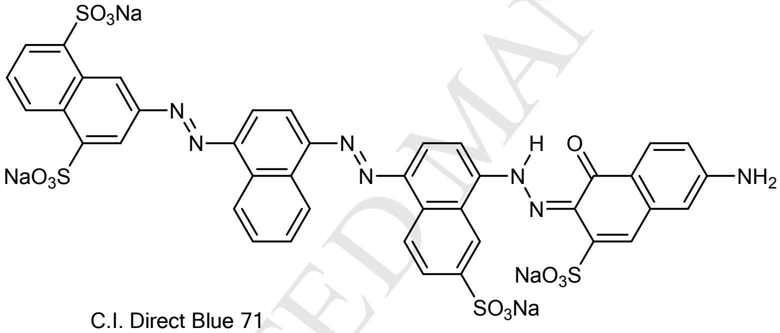


Figure 3 Effect of calcined Na_2SO_4 on the uptake of direct dyes on cotton; 1% omf dye; 90°C; 1:60 liquor ratio; plotted using data from (22)

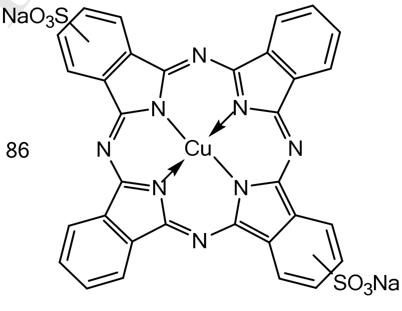
The vast majority of direct dyes are non-metallised, dis-, tris- and poly-azo structures, although metallised azo dyes as well as a few non-azo dye classes are represented, as exemplified by C.I. Direct Yellow 59, C.I. Direct Blue 71 and C.I. Direct Blue 86 [eg (23-26)].



C.I. Direct Yellow 59

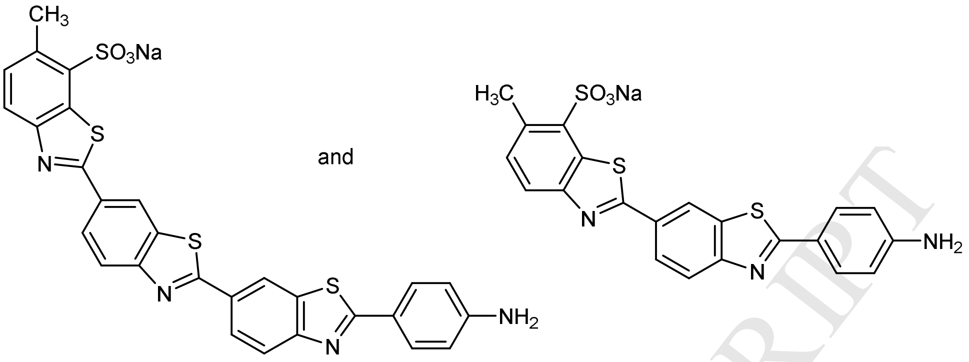


C.I. Direct Blue 71



C.I. Direct Blue 86

Structurally, modern azo direct dyes bear an uncanny resemblance to the first member of this dye particular class, *Congo Red* (C.I. Direct Red 28) [which nowadays enjoys little usage because of the low fastness displayed by the dye on cellulosic fibres], insofar as one or more of the substituted aromatic rings carry sulfonate groups that confer water-solubility upon the dye molecules; generally, modern non-azo direct dyes also tend not to stray too far from this well-trodden, structural path.

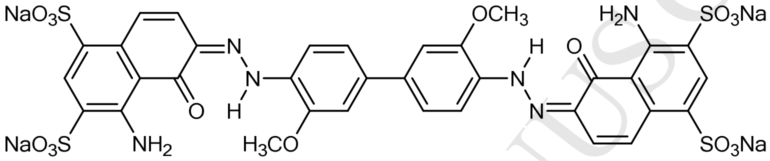


C.I. Direct Yellow 59

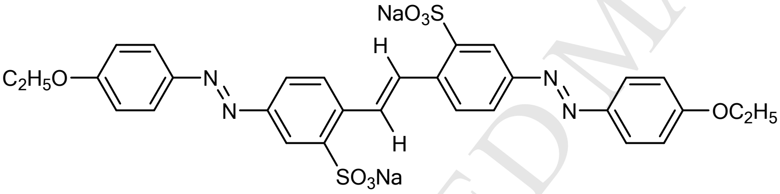
As such, direct dyes are, in essence, long, planar, anionic molecules that are solubilised by one or more sulfonate/sulfonic acid groups (commonly as the Na salt).

This brief excursion into the fundamental structural features of direct dyes enables an initial, cursory response to be given to the question posed by the title of this section, namely *why is inorganic electrolyte used in the dyeing of cellulosic fibres with direct dyes?* Essentially, the addition of either NaCl or Na_2SO_4 to a direct dye dyebath increases the inherent low substantivity displayed by direct dyes towards cellulosic fibres with the result that dye uptake is promoted. As dicussed later in this paper, the reasons why direct dyes display low substantivity in the absence of added electrolyte and, also, why added electrolyte so effectively promotes dye uptake, stem from the dye's distinctive architecture, namely the presence of one or (most usually) more sulfonate groups which impart both water solubility and anionicity, couped with with their long, linear structure.

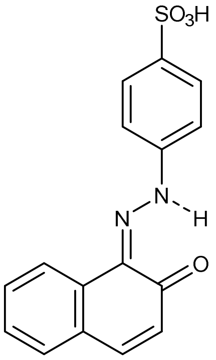
From the viewpoint of the nature of the interactions between direct dyes and cellulosic substrates in the presence of added electrolyte, just as the chemistry of direct dyes has witnessed few major developments since their commercial introduction some 130 or so years ago, so too, theoretical studies concerning the physicochemical mechanism of direct dye adsorption on cellulosic fibres have enjoyed only modest elaboration since the advent of the first elegant, detailed studies in the early 1930's and subsequent investigations over the next decade or so, which formed the basis of the above mentioned SDC classification system for direct dyes [eg (8, 22, 27-36)]. Indeed, our current understanding of the thermodynamics and kinetics of direct dye adsorption on cellulosic fibres is mostly based on work carried out using remmarkably very few, usually purified direct dyes (ie non-commercial grade samples), as exemplified by the tetrasulfonated C.I. Direct Blue 1 and disulfonated C.I. Direct Yellow 12 and C.I. Direct Red 2, all of which nowadays enjoy limited industry usage because of fastness limitations. As discussed in section 5.4, despite considerable attention, the precise nature of the mechanism of adsorption of direct dyes on cellulosic fibres has not been adequately resolved.



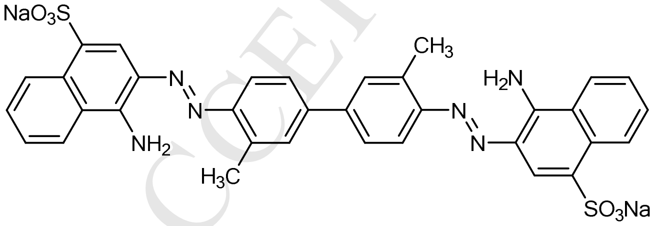
C.I. Direct Blue 1



C.I. Direct Yellow 12



C.I. Acid Orange 7



C.I. Direct Red 2

As recounted above, characteristically, direct dyes typically contain several sulfonate groups, which confer commercially acceptable levels of water solubility. As the aqueous solubility of direct dyes is difficult to determine accurately owing to practical difficulties of separating the dissolved solute from the saturated solution (37), unsurprisingly, the effect of added electrolyte on the aqueous solubility of direct dyes (as well as that of anionic dyes in general) has received modest attention.

Nonetheless, it has been reported that the solubility of purified C.I. Direct Blue 1 and purified C.I. Direct Yellow 12 was markedly reduced in the presence of NaCl (Table 2), a similar finding being made in the case of purified C.I. Acid Orange 7 in the presence of both NaCl and Na_2SO_4 at 25°C (38).

Table 2 Solubility of purified C.I. Direct Blue 1 and C.I. Direct Yellow 12 (39)

dye	Temperature/°C	NaCl/ gl^{-1}	solubility/ gl^{-1}
C.I. Direct Blue 1	50	0	6.18
		2	3.49
		4	2.30
		10	1.88
		40	0.85
C.I. Direct Yellow 12	35	0	7.61
		2	1.47
		4	0.19
		10	0.069
		20	0.024
		40	0.015
	45	4	1.412
		10	0.225
		20	0.086
		40	0.039
		60	0.025

The solubility of commercial direct dyes ranges from ~5 to 200 gl^{-1} at 98°C (40) and is increased by increases in both temperature (39, 41) and pH (40). Although such a high level of aqueous solubility is the major reason for the celebrated simplicity and inherent robustness of the exhaust direct dyeing process, the characteristic high solubility of direct dyes is of far more fundamental significance in terms of their application to cellulosic fibres, insofar as, it is responsible not only for the dye's inherent low substantivity towards cellulosic fibres but also is the reason why added inorganic electrolyte is so effective in promoting dye uptake. Another corollary of the high aqueous solubility of direct dyes is that the amount of water employed in immersion dyeing, as expressed by liquor ratio, has a remarkably pronounced effect on both the rate and extent of direct dye uptake; importantly, liquor ratio also influences the effectiveness with which added electrolyte promotes dye uptake. As such, the particular liquor ratio that is utilised in direct dye application is of crucial significance as it directly influences the level of substantivity displayed by the direct dye towards the substrate within the dye-electrolyte-fibre dyeing system. This is because liquor ratio not only determines the amount of water available in the dyebath for dye dissolution and, thus, the amount of dye adsorbed by the fibre, but it also governs the effective dye concentration within the dyebath and, therefore. the relative intensity of the dye-electrolyte interactions that result in dye uptake.

Indeed, in commercial immersion procedures for applying direct dyes to cellulosic fibres, the level of substantivity displayed by the dye towards the cellulosic substrate is manipulated by the dyer so that uniform dyeings of the required depth of shade are secured within the allotted dyeing time. This is achieved by regulating the amount of inorganic electrolyte that is added to the direct dye dyebath in cognisance of the particular liquor ratio used for dyeing. Thus, a given amount of added inorganic electrolyte is used in combination with a particular liquor ratio (and at a given temperature), so that the relative contributions which added electrolyte and liquor ratio each make towards dye-fibre substantivity are strictly controlled. If the liquor ratio utilised for dyeing is changed then the amount of added electrolyte employed for dyeing must be altered accordingly, so as to achieve a particular level of dye-fibre substantivity that is consistent with producing uniform dyeings of the desired depth of shade (within the prescribed time frame).

The substantivity of a direct dye towards a particular cellulosic fibre, and, thereby, the extent of dye uptake achieved, can therefore be conveniently controlled by adjusting the amount of water in the dyebath (ie altering the liquor ratio employed for dyeing) and/or adjusting the amount of added inorganic electrolyte in the dyebath. Hence, the two seemingly disparate facets of direct dyeing, namely the amount of added electrolyte used and the liquor ratio employed for dyeing, each influence dye substantivity and, thereby, dye uptake. In terms of the physical attributes of direct dyes that might be affected both by liquor ratio and electrolyte, the most likely contender is the aqueous solubility of the dye.

Unfortunately, despite the fact that the effect of liquor ratio on dye uptake in immersion dyeing processes in general is a much studied subject, and the role of liquor ratio in direct dyeing has attracted considerable attention, the promotional effect of reducing the liquor ratio utilised in dyeing on direct dye uptake has not been adequately described in terms of currently accepted dyeing theory, namely, in terms of the physico-chemical mechanism by which direct dyes are adsorbed on cellulosic substrates. Furthermore, the vitally important combinatorial nature of the effects of liquor ratio and added inorganic electrolyte on direct dye uptake has not been addressed from the viewpoint of the mechanism of direct dye adsorption on cellulosic fibres. Indeed, as discussed below, in order to understand the mechanism by which added electrolyte promotes direct dye uptake on cellulosic fibres, it is also necessary to elucidate the mechanism by which liquor ratio influences dye uptake.

Consequently, in terms of the question posed by the title of this section *why is inorganic electrolyte used in the dyeing of cellulosic fibres with direct dyes?*, the simple answer is because the added electrolyte reduces the aqueous solubility of the dye in the dyebath. As discussed below, reduction in dye solubility imparted by adding electrolyte to a direct dyebath can also be achieved by, and is analogous to, reducing the liquor ratio used for dyeing.

4 why has the use of inorganic electrolyte in the dyeing of cellulosic fibres with direct dyes not been eradicated?

Without wishing to be overly sceptical, it appears that the dyeing industry must consider inorganic electrolyte as entirely indispensable in the exhaust dyeing of cellulosic fibres using direct dyes, reactive dyes, etc., since there doesn't seem to be any industry-led strategy to stop using NaCl or Na_2SO_4; furthermore, attempts to reduce the amount of electrolyte used in dyeing can, at best, be described as modest. In contrast, wastewater treatment professionals and environmental authorities will likely, and rightly, contend that the use of either NaCl or Na_2SO_4 in cellulosic fibre dyeing is entirely unacceptable and only the elimination of such environmentally objectionable compounds from cellulosic dyeing is appropriate.

Indeed, the neutral observer can be excused for thinking that the use of either NaCl or Na_2SO_4 in cellulosic fibre dyeing is, and always has been, acceptable, since, if this were not the case, then surely, over the past 130 or so years since the commercial introduction of direct dyes, dye makers would have developed direct dyes that did not require the use of added inorganic electrolyte. Unfortunately, commercial developments in both dye chemistry and dye application were instead directed towards overcoming the major end-use deficiency of direct dyes, namely their inherent very poor wet fastness properties on cellulosic fibres, with the upshot that the (severe) environmental and economic problems posed by using inorganic electrolyte in the dyeing of cellulosic fibres with direct dyes remain to the present day. The developments in dye chemistry and dye application alluded to above were, nonetheless, remarkable, as they combined outstanding research in dye chemistry and remarkable innovation in dye application that resulted in the commercial introduction of reactive dyes for cellulosic fibres in the mid-1950's. Indeed, the ingenuous elegance of the dyeing process that was developed to apply this new type of dye to cellulosic fibres enabled the dyes to form a covalent bond with the cellulosic substrate, so that the newly-introduced *reactive dyes* displayed outstanding levels of fastness to wet treatments (washing, perspiration, water, etc.) on cellulosic fibres, and, as such, overcame the inherently very low wet fastness properties exhibited by direct dyes on such fibres.

However, the problem of added electrolyte in cellulosic dyeing was not diminished by the introduction of reactive dyes. The majority of reactive dyes are non-metallised, mono- and dis-azo compounds, although metallised azo dyes and several non-azo types are available. In a reactive dye, the azo (or other type of) chromogen contains one or more substituted aromatic rings that carry one or (most commonly) more sulfonate/sulfonic acid groups; attached to the chromogen is a reactive system that enables the dye to form a covalent bond with the cellulosic substrate during dyeing. Structurally, reactive dyes are long, planar, anionic molecules, solubilised by one or more ionised sulfonate groups, and, as such, reactive dyes bear a very close structural resemblance to direct dyes. Indeed, such is the closeness of this architectural similarity, that prior to the reactive dye forming a covalent reaction with the cellulosic fibre (ie in the absence of dye-fibre reaction), the adsorption of reactive dyes onto cellulosic fibres is considered to occur in a manner analogous to that of direct dyes (2). Thus, added inorganic electrolyte is used to promote the uptake of reactive dyes on cellulosic fibres. Unfortunately, the amount of NaCl or Na_2SO_4 required to promote uptake of reactive dyes on cellulosic fibres is several orders greater than that typically employed for direct dyes (Table 1). As reactive dyes are nowadays by far the most popular class of dye used for dyeing cellulosic fibres (Figure 1) and this popularity has resulted in worldwide consumption of direct dyes (and that of the other three classes of dye for cellulosic fibres) having declined, it is not only unfortunate but more importantly, unacceptable, that the severe problems posed by the use of added NaCl or Na_2SO_4 in cellulosic fibre dyeing using direct dyes were exacerbated, rather than alleviated, because of the introduction and global popularity of reactive dyes. Subsequent parts of the paper will report investigations of the role of added inorganic electrolyte in the application of both commercial grade and purified reactive dyes to cotton.

From the perspective of eliminating added inorganic electrolyte in cellulosic fibre dyeing, attempts have been made to enhance the inherent low substantivity displayed by direct dyes and other anionic dyes towards cellulosic fibres, by pre-treating the substrate prior to dyeing so as to introduce either quaternary amines or aliphatic amino groups (amination) in the fibre. Although such cationisation (quaternary amines) and amination (aliphatic amino groups) pre-treatments have received attention over several decades [eg (26, 42-46)], neither of the approaches enjoy general commercial success, for a variety of reasons, that include, for example, alteration of hue, and the tendency of such pre-treatments to promote ring dyeing and reduced fastness to light and rubbing.

Whilst it is unlikely that any dyeing industry practitioner would deny that the use of NaCl or Na_2SO_4 in cellulosic fibre dyeing is environmentally unacceptable, large amounts of these inorganic electrolytes continue to be routinely employed commercially in the immersion application of direct dyes (and reactive dyes) to cellulosic fibres. Sadly, given the current gaps in our knowledge of the role of NaCl and Na_2SO_4 in such dyeing processes, this situation seems unlikely to change without fundamental advances in our understanding of the highly complex function of added electrolyte in such dyeing processes. Furthermore, as discussed below, in order to understand the mechanism by which added electrolyte promotes direct dye uptake on cellulosic fibres, it is also necessary to elucidate the mechanism by which liquor ratio influences dye uptake, so that the vitally important combinatorial nature of the effects of liquor ratio and added inorganic electrolyte on direct dye uptake can be resolved.

5 current views of the role of added electrolyte in the dyeing of cellulosic fibres using direct dyes

As recounted, although the mechanism by which added electrolyte promotes both the rate and extent of uptake of direct dyes (and other dye anions) onto cellulosic fibres has received considerable attention [eg (9, 30, 32, 33, 35, 47-56); see (2) for a summary], our understanding of this highly complex subject leaves much to be desired. However, such a situation deserves to be placed in context.

In essence, whilst the structure of liquid water (as well as that of the other three physical forms of water namely, solid, vapour and supercritical fluid) has enjoyed extensive investigation over a long period of time and a great many water models have been proposed, the precise structure of liquid water is still not entirely resolved. Furthermore, although the interactions between electrolytes (including NaCl and Na_2SO_4) and liquid water have also received significant examination over many decades within several scientific disciplines, the exact nature of such interactions are not fully understood. Consequently, a variety of mechanistic theories have been suggested for electrolyte-water interactions and several systems have been developed that seek to classify ions according to their effects on the three-dimensional, H-bonded structure of liquid water (ie as either structure-making or structure-breaking ions) or their ability to precipitate proteins, as exemplified by the Hofmeister series (2).

Hopefully, this, necessarily very brief, discussion of our current understanding of the highly complex areas of water structure and water-electrolyte interactions goes some way to explain why the mechanism by which added electrolyte promotes both the rate and extent of uptake of direct dyes (and other dye anions) onto cellulosic fibres is not fully resolved.

As intimated above, because of the importance of added inorganic electrolyte in the dyeing of cellulosic fibres, the effects which NaCl and Na_2SO_4 have upon direct dye uptake (and that of other types of dye anion) have been studied by many workers and manifold theories have been proposed to explain the promotional effect exerted by added electrolyte on the uptake of anionic dyes on cellulosic fibres that favour/disfavour, for example, electrical repulsive effects, dye solubility, colloidal stability, electrostatic effects, water structure changes, increased water imbibition and dye aggregation. Of these theories, three have attracted most discussion, namely, that the added inorganic electrolyte influences:

- electrical repulsion effects between dye anions and the negatively charged fibre;
- the state of aggregation of the dye in solution;
- the solubility of the dye in the solution.

However, as mentioned, none of these (or other) theories adequately explains the promotional effect of added electrolyte on direct dye uptake in terms of the currently accepted mechanism by which the dyes are adsorbed on cellulosic fibres. In the following sections, the above three most popular mechanistic theories are discussed in terms of a re-analysis of experimental observations reported by several workers as a means of developing a theoretical model of the mode of action of added inorganic electrolyte on direct dye uptake.

5.1 electrical repulsion effects

As cellulosic fibres acquire a negative charge when placed in water (as do all other common types of textile substrate) it is widely held that this charge is lowered in the presence of electrolytes such as NaCl and Na_2SO_4, and, as a consequence, long-range repulsive forces operating between the negatively charged cellulosic fibre surface and the negatively charged direct dye anions in the dyebath are reduced, thereby resulting in promotion of dye uptake. It has been suggested that according to this particular concept, it should not be possible to dye cellulosic fibres using anionic dyes in the absence of added electrolyte, as exemplified by Knecht and Batey (57), who recorded in 1909 that for many direct dyes, dyeing did not occur in the absence of added electrolyte. Such early views were subsequently confirmed in detailed studies undertaken using purified direct dyes on cellulosic substrates (8, 36, 58), as illustrated by the results shown in Figure 4 for C.I. Direct Blue 1 and C.I. Direct Red 2.

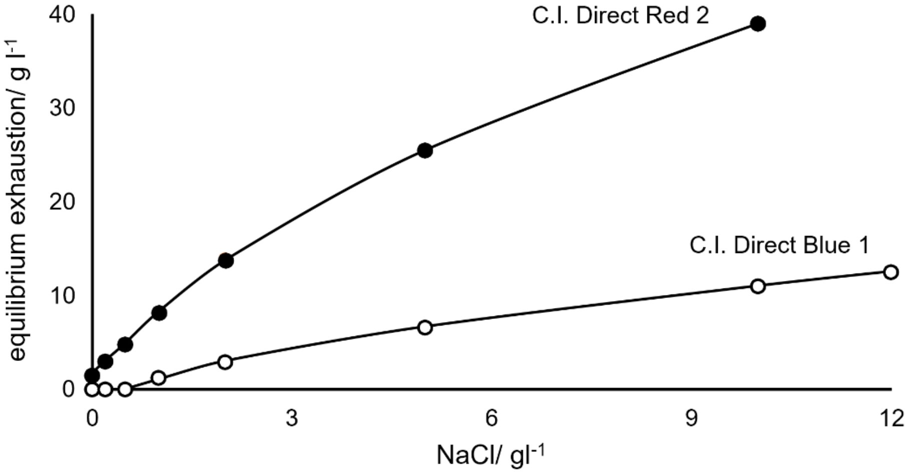


Figure 4 effect of NaCl on uptake of purified direct dyes on CV film; 101°C; 0.05 gl^{-1} dye; plotted using data from (36)

The lack of dye uptake in the absence of added electrolyte was attributed (35, 59, 60) to the high negative potential of the cellulosic fibre surface having prevented sorption of the dye anions. Indeed, it was proposed (54, 60) that pure direct dyes display zero or negligible substantivity towards cellulose because of repulsion between the like (anionic) charges on the dye and substrate.
However, several purified direct dyes display meaningful substantivity towards cellulosic fibres when applied to in the absence of added electrolyte (32, 33). From observations that dye uptake in the absence of added electrolyte occurred in the case of the dibasic dye C.I. Direct Yellow 12 (32), it was concluded that the effect was related to dye basicity (33, 58). An alternative view (2) sought to link the extent of dye uptake achieved in the absence of added electrolyte to the aqueous solubility of the dyes and their aggregation behaviour in solution, insofar as high solubility direct dyes such as the tetrasulfonated C.I. Direct Blue 1 will tend to display a corresponding low propensity to aggregate in solution and, as a corollary, will likely exhibit lower uptake than dyes of lower aqueous solubility, such as the dibasic dyes C.I. Direct Red 2 and C.I. Direct Yellow 12. Thus, whilst some pure direct dyes may exhibit little if any substantivity towards cellulosic fibres in the absence of added electrolyte, other dyes may well display meaningful uptake and such difference in dyeing behaviour will likely result from structural characteristics, such as their aqueous solubility. Indeed, as will be discussed in subsequent parts of this paper, cotton and other cellulosic fibres can be dyed to commercially realistic depths of shade using both pure and commercial anionic dyes in the complete absence of added inorganic electrolyte.

In the context of the surface potential of cellulosic fibres, it is widely held that *zeta potential* (ζ-potential), which is an experimentally determinable attribute of the electric double layer [see (2) for a discussion], can furnish information regarding electrostatic interactions between charged surfaces and particles (ie fibres and dyes) that arise from overlap of their respective electric double layers under aqueous conditions. Characteristically, cellulosic fibres exhibit a pH-dependent, negative ζ-potential in aqueous solution [eg (61, 62)] that arises from the presence of ionised carboxyl groups (ie $–COO^-$) in the substrate, the distinctive plateau in zeta potential within the alkaline pH region being attributable to complete dissociation of these acidic groups. In this context, whilst cellulose contains a very large amount of ionisable hydroxyl groups, which, theoretically, could contribute to the pH-dependent zeta potential displayed by cellulosic fibre surfaces in aqueous solution, the negative zeta potential of cellulose materials is commonly attributed only to the presence of $-COO^-$ groups.

Neale and Peters (63) first demonstrated that the negative surface potential developed at a cotton fibre surface decreased in the presence of increasing amounts of added NaCl as well as other inorganic monovalent electrolytes. However, analysis (2) of this data revealed that the relatively low amount of added monovalent electrolyte that would be needed to ‘neutralise’ the negative surface potential on the cotton fibre surface by the adsorption of an equivalent number of Na^+ cations from the added electrolyte, represented only a small proportion of the amount of added electrolyte that is typically utilised in dyeing cotton (and other cellulosic fibres) with anionic dyes such as direct dyes, and especially, reactive dyes. Furthermore, in terms of the notion that added electrolyte ‘neutralises’ the negative surface charge of cellulosic fibres in aqueous solution, it was argued that, even if it was assumed that the negative surface charge developed in the cellulosic substrate arose from ionisation of **all** potentially ionisable groups in cellulose (ie both -COOH and -OH groups) then the amount of added NaCl that would achieve ‘neutralisation’ of all of these accessible, completely ionised acidic groups in cellulose (ie both $-COO^-$ and $-O^-$) was much lower than that typically employed in the application of, for example, reactive dyes to cotton (2). In view of the difference in the amounts of added electrolyte, such as NaCl, that would be required theoretically to achieve ‘neutralisation’ of surface charge and those typically utilised in practical dyeing, it was concluded (2) that the role of added electrolyte in promoting anionic dye uptake on cellulosic fibres cannot simply be attributed to reduced fibre surface charge.

Thus, despite the widely held view that added electrolyte promotes anionic dye uptake on cellulosic fibres by reducing electrical repulsion between the dye anions and the negatively charged cellulosic fibre, additional/alternative explanations have been proposed. For example, in 1958, Boulton (54) proposed a two-stage mechanism in which the added electrolyte initially suppresses repulsive forces operating between the dye and the cellulosic fibre surface and, thereafter, further added electrolyte lowers the solubility of the dye and shifts dye adsorption in favour of the fibre. A more recent analysis of publications relating to the role of inorganic electrolyte in cellulosic fibre dyeing (2) suggested that a dual-mode mechanism likely applies, in which the added NaCl or Na_2SO_4 promotes dye aggregation and/or reduces the aqueous solubility of the dye in the dyebath and also lessens the repulsive forces that are present between the dye anions and the negatively charged cellulosic fibre surface under aqueous conditions. In proposing this particular dual-mode mechanism (2), it was considered that because of the marked propensity of direct dyes to aggregate in aqueous solution, reduced dye solubility resulting from increased dye aggregation was likely to be of more significance than lessening of dye-fibre repulsion effects.

5.2 dye aggregation/dye solubility effects in solution

Most chemical classes of dye display a pronounced predisposition to aggregate in aqueous solution whereby identical dye molecules/dye ions or molecules/ions of different dyes associate, forming aggregates that comprise dimers and higher aggregates; indeed, dye self-association is a commonly encountered phenomenon in immersion dyeing processes. The tendency of dye molecules to aggregate is a consequence of the structural features of the amphiphilic molecules, notably the presence of phenyl rings and the ability to adopt a planar structure, and is influenced by several dyebath elements including liquor ratio, temperature and dyeing auxiliaries, including surfactants and, most notably, inorganic electrolytes. Dye aggregation in solution is an especially well-researched phenomenon and many review articles are available, owing to its application in many areas other than textile dyeing [eg (64-78); see (2) for a brief summary].

As mentioned, characteristically, direct dyes are long, planar molecules that carry sulfonate/sulfonic acid groups (as exemplified by the dye structures presented above) as a result of which, they are characterised by a distinct propensity to aggregate in aqueous solution via coplanar association; indeed, evidence suggests that several direct dyes, such as C.I. Direct Blue 1 and C.I. Direct Red 28, aggregate in aqueous solution even in the absence of added electrolyte (79, 80). The innate predisposition of direct dyes to self-associate in solution is encouraged at high dye concentrations as well as by the addition of electrolyte, but is reduced by increasing temperature. The ability of electrolytes such as NaCl to induce aggregation of direct dyes in aqueous solution is a readily-observed phenomenon in which, typically, increasing amounts of added electrolyte initially induce turbidity within the aqueous dye solution and, eventually, precipitation of the dye. The amount of electrolyte required to flocculate direct dyes from aqueous solution varies for different dyes and for different types of electrolyte (37). Neale and Stringfellow (34) sought to establish whether direct dye uptake on cellulosic materials reached a limiting value at high amounts of added electrolyte, prior to electrolyte-induced precipitation of the dye. Using purified C.I. Direct Blue 1 and CV film, these workers observed that at an initial concentration of 1 gl^{-1} dye and ≤100 gl^{-1} added NaCl, dye uptake increased rapidly and then remained reasonably constant (Figure 5).

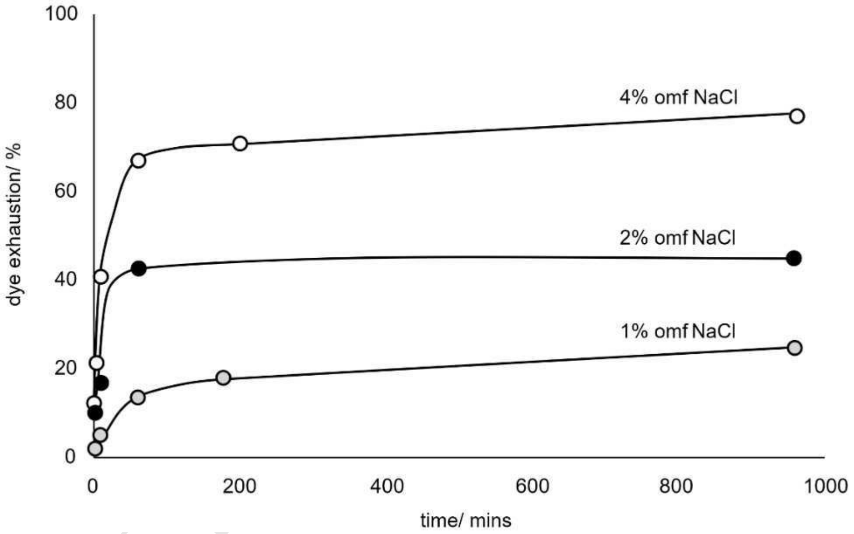


Figure 5 Effect of electrolyte on uptake of 1 gl^{-1} purified C.I. Direct Blue 1 on CV film at 90^{o}C; plotted using data from (34)

At higher electrolyte concentrations, initial dye uptake proceeded more slowly and, even after prolonged dyeing times, uptake continued to increase slowly. These workers (34) suggested that up to an electrolyte concentration of 100 gl^{-1} the dye was in molecular dispersion whereas at higher amounts of added electrolyte, dye aggregates formed. Whilst aggregation did not result in visible dye precipitation at the dyeing temperature used (90^{o}C), it was assumed that dye aggregation impeded dye diffusion within the CV film, resulting in slower initial rates of dye uptake (34). It was also considered (34) that at high amounts of added electrolyte, the dye likely became deposited as multi-molecular layers either within or on the film, a situation that would account for the observed slow increase in dye uptake (Figure 5).

The phenomenon can be considered to arise as a consequence of the long, linear structure of the dye molecules and the presence of sulfonate/sulfonic acid groups. The outstanding ability of NaCl and Na_2SO_4 to induce direct dye self-association in aqueous dyebaths can be attributed to the added inorganic electrolyte ions promoting hydrophobic interaction between planar aromatic regions in adjacent direct dye molecules.

In effect, dye aggregation is favoured because the counterions (ie Na^+) derived from the added inorganic electrolyte screen the anionic charge (usually derived from $-SO_3^-$ groups) on the dye anions, thus reducing electrostatic repulsion between neighbouring charged dye anions, which promotes dye-dye interactions that favour dye self-association. In this context, the electrolyte ions act as kosmotropes (small, high charge density ions that bind water molecules strongly) (2) which impart conformational changes to the dye molecules that promote hydrophobic interaction between the planar aromatic rings in neighbouring dye molecules; it seems likely that the π-π interactions between aromatic regions in the dye molecules will be expedited by the screening of the anionic charge on the dye anions by the electrolyte counterions. Several workers favour the notion that hydrophobic interaction contributes to dye self-association in solution [eg (2, 81-83)], which seems reasonable in view of the planar nature of direct dye anions and the likelihood of π-π interactions operating between aromatic centres within neighbouring dye molecules. The driving force for such hydrophobic interaction, of which dye aggregation is a consequence, is the need for the surrounding water molecules to minimise their interaction with the amphiphilic direct dye solutes, so that disruption of the surrounding water structure by the dye molecules is minimalised.

Because of the strong dye-dye interactions between neighbouring dye molecules and the screening of the -SO_3^- groups by the Na^+ counterions, ionisation of the direct dye molecules will be supressed and, therefore, the dye molecules that are present within the dye dimers, trimers, *n*-mers, etc. will possess lower aqueous solubility than their monomolecular direct dye counterparts within the aqueous dye solution in the dyebath. Furthermore, as the amount of water in the dyebath that is available to the dye aggregates will be reduced because of hydrophobic interaction, so that the aggregates will likely combine to form particles that will constitute a dye dispersion within the aqueous dyebath. Thus, because of electrolyte-induced dye self-association, the concentration of dye in solution in the dyebath will be reduced; therefore, the addition of NaCl or Na_2SO_4 to a direct dye in solution reduces the solubility of the dye, as indeed has been observed (Table 2). As the suppression of dye solubility imparted by added inorganic electrolyte will increase with increasing amounts of added electrolyte, so the extent of electrolyte-induced dye aggregation will also increase with increasing amount of electrolyte, as observed in practice (30, 84, 85), with the result that, at sufficiently high amounts of added electrolyte, dye precipitation will likely occur, as again, has been recorded (34). In effect, the process of applying direct dyes in the presence of added inorganic electrolyte is akin to controlled dye precipitation onto the cellulosic substrate, insofar as the amount of added electrolyte is adjusted so as to induce the formation of a dispersion of dye particles in the aqueous dyebath whilst avoiding flocculation of the dye.

In view of the marked proclivity of direct dye molecules to aggregate in solution, it is of course possible that for some direct dyes, self-association and, thus, reduced aqueous solubility, may occur in the absence of added electrolyte, as has been observed (79, 80). Since, as mentioned, because the predisposition of direct dyes to self-associate in solution is encouraged at high dye concentrations, it follows that such concentration-induced aggregation is a likely consequence of reducing the liquor ratio used for dyeing; this is discussed in the next part of the paper.

Many workers consider that such observations explain the nature of the promotional effect of added electrolyte on direct dye uptake, as exemplified by the previously mentioned Knecht and Batey (30), who proffered that added electrolyte ‘salted out’ direct dyes from aqueous solution, resulting in precipitation of the dye in the fibre, or, in the absence of precipitation, the added inorganic electrolyte induced dye aggregation. However, although electrolyte-induced dye aggregation may well seem to offer a reasonable explanation as to why added inorganic electrolyte promotes direct dye aggregation, this physical act of dye molecule self-association in solution cannot be described using the currently accepted physico-chemical mechanism (which is discussed in section 5.4) by which direct dyes are adsorbed on cellulosic fibres.

5.3 dye aggregation/dye solubility effects in the fibre

Whilst the above discussion relates to the promotional effects imparted by added inorganic electrolyte in terms of electrolyte-induced dye aggregation in solution, the possible effects of added electrolyte on the physical state of the dye within the fibre merits consideration. In this context, dye aggregates within dyed fibres have been identified for several dye-fibre systems [see (2) for a summary], including cellulosic fibres dyed using direct dyes (86-88), reactive dyes (89), azoic colorants (86, 90) and vat dyes (91). Furthermore, from the viewpoint of cellulosic fibre dyeing, it has been proposed (92) that direct dye aggregates concentrate at the fibre-dyebath interface and, subsequently, additional self-association of the adsorbed dye molecules takes place within the fibre in the form of either aggregates or micelles; the dimeric form of C.I. Direct Blue 1 in CV sheet was found to be of the same shape as that in solution (93). In contrast, it has been suggested that dye adsorption proceeds without the formation of aggregates (94) and, also, that dye aggregates present in solution are broken up upon adsorption onto cellulosic fibres (93). Other workers suggest that direct dyes are adsorbed by cellulosic fibres in monomolecular form and subsequently aggregate after the associated water of solvation has been removed (95).

Such contradictory findings highlight the fact that our understanding of the self-association of all types of dye, including direct dyes, within textile fibres leaves much to be desired; indeed, the physical state of dyes in solid materials in general has received much less attention than in solution, mainly because of experimental difficulties. Nevertheless, although relatively little is known about the nature of dye self-association within fibres and the interactions that might occur between such dye particles and the component polymer chains within fibres, it has been suggested (2) that dye aggregation may well be a common occurrence within dyed substrates because of the inherent planarity and amphiphilicity of dye molecules in general.

As an aqueous environment is utilised in immersion dyeing processes, all of the essential components of the direct dye/electrolyte/cellulosic fibre system will be hydrated, namely the dye, inorganic electrolyte and the fibre. It follows, therefore, that during aqueous dyeing, the fibre is immersed in and contains dyebath solution that comprises both dye and added electrolyte. Thus, the effects of added electrolyte on the self-association of direct dye molecules in solution extends to all parts of the direct dye/electrolyte/fibre system, including dyebath solution present within the interstitial regions of the fibre. Accordingly, irrespective of both the nature of the physical state in which direct dye molecules are adsorbed by cellulosic fibres (ie whether in monomolecular form or as aggregates, micelles, etc.) and the manner by which the dye molecules diffuse within the substrate (as discussed in section 5.5), the effect of the added inorganic electrolyte on the physical state of the direct molecules in the dyebath will extend to the proportion of the dyebath that resides within the substrate. Therefore, the state of the dye molecules as detected in a dyed substrate at the end of dyeing may or may not reflect that which prevails in the dye solution during aqueous dyeing. This situation would go some way to explain why our understanding of the physical state of dyes in solid materials is far from extensive and also, that the findings of studies often are contradictory.

5.4 thermodynamics of dyeing

In essence, thermodynamic analysis of dyeing processes involves measuring the distribution of a dye between the fibre phase and the solution phase (ie the dyebath) at a given, constant temperature (ie under isothermal conditions) when the immerison dyeing system is at equilibrium. As such, the thermodynamics of dyeing provides a quantitative description of the propensity of the dye to transfer from the solution phase to the fibre phase. The ensuing equilibrium adsorption isotherm data, such as that displayed in Figure 6, is then interpreted in terms of its correlation with a particular isotherm equation, so that the physic-chemical mechanism of dye adsorption can be established.

In simple terms, the aqueous dyeing process is heterogeneous in that it comprises a fibre phase which, at the start of dyeing, comprises the textile substrate, as well as an aqueous phase that comprises dye solution. When undyed fibre is placed in an aqueous dyebath, dye molecules spontaneously move from the aqueous phase (dyebath) to the solid phase (fibre).

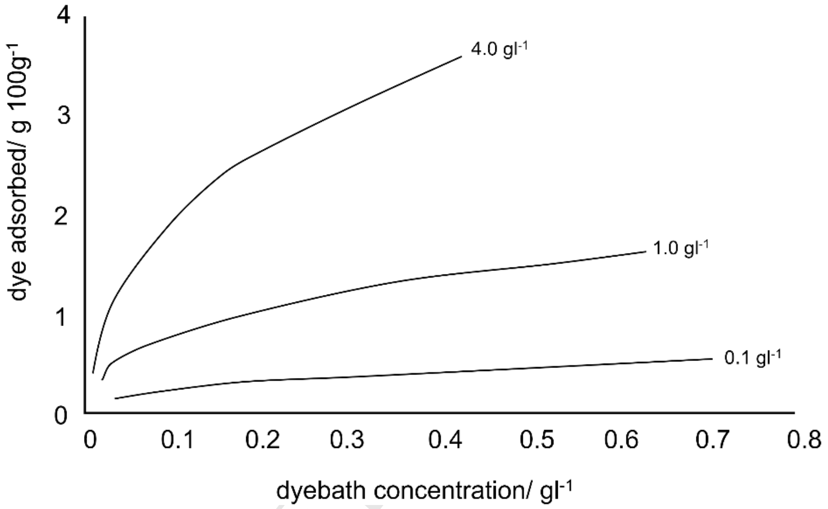


Figure 6 Adsorption isotherms for C.I. Direct Yellow 12 on CV sheet at 40^{o}C in the presence of different amounts of NaCl (drawn using data from (32))

Dyeing continues until either all of the dye in the dyebath has transferred to the substrate or until an equilibrium is achieved wherein dye molecules constantly exchange between the aqueous phase and fibre phase and the process of dye adsorption onto the fibre and the process of dye desorption from the fibre are equal. Once equilibrium has been achieved, the partition of the dye between the fibre phase and the solution phase is described by Eq 1, 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 (see the Appendix for a discussion of the consequences of using the same or different units for measuring values of $[D]_f$ and $[D]_s$).

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

In Eq 1, K is the equilibrium partition coefficient which describes the distribution of the dye between the dyebath, s and fibre, f, phases; the higher the value of K 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. The predisposition of the dye to partition between the fibre and solution phases is commonly expressed in terms of the thermodynamic standard affinity of the dye, $-\Delta\mu^{\theta}$, which is calculated from the equilibrium dye adsorption data, using an equation that takes the form of some or other mathematical interpretation of Eq 1.

As mentioned, although the equilibrium adsorption of direct dyes on cotton and other cellulosic substrates has received considerable attention from many researchers over a long period of time, the precise nature of the mechanism by which such adsorption on cellulosic fibres occurs has not been fully elucidated [see, for example (2, 58, 96-98) for accounts]. In recent times, the removal of direct dyes (as well as that of other anionic dyes including reactive dyes) from dyeing wastewater by adsorption onto various cellulosic substrates has also attracted much research activity, and the mechanism by which such adsorption proceeds has received interest [eg (99, 100)].

5.4.1 adsorption isotherms

As recounted, the search to find the mechanism by which direct dyes are adsorbed on cellulosic fibres began in earnest in the 1930’s, taking the form of, often elegant, detailed studies of dye sorption onto various types of cellulosic materials. The equilibrium adsorption of direct dyes onto cellulosic substrates is most commonly interpreted using a Freundlich-type isotherm equation (2). According to the IUPAC system of classification of adsorption isotherms (101), the characteristically sigmoidal-shape of the Freundlich isotherm is representative of unrestricted monolayer-multilayer adsorption at non-specific sites within the cellulosic material and describes adsorption on macroporous adsorbents that involve weak and strong intermolecular interactions. In terms of direct dye adsorption on cellulosic fibres proceeding via a Freundlich-type mechanism, as represented by the data shown in Figure 6 (32), the initial stages of dye adsorption that result in the formation of monolayers of adsorbed dye molecules is indicative of the adsorption of monomolecular dye ions. The subsequent formation of multilayers of adsorbed dye molecules at non-specific sites in the fibre is symptomatic of self-association of adsorbed dye molecules within the fibre: for example, adsorbing dye molecules may associate with previously adsorbed molecules within the substrate or aggregated dye molecules from the dyebath may be adsorbed. Dye aggregation within the fibre and, thus the formation of multilayers of adsorbed dye, seems likely, in view of the previously discussed marked tendency of the long, planar, direct dye molecules to self-associate in solution via π-π interactions between neighbouring dye molecules, and the promotional effect of added inorganic electrolyte on aggregation and suppression of dye solubility.

However, several workers have found that the equilibrium adsorption data secured for direct dyes on cellulosic fibres better correlates with an IUPAC type 1 or Langmuir-type equation [see (2)] which describes adsorption on microporous adsorbents via the formation of a monolayer on a fixed number of specific sites (101). Thus, in contrast to the Freundlich-type adsorption mechanism, adherence of direct dye adsorption to a Langmuir-type model requires that the cellulosic fibre contains a limited number of specific sites at which the direct dye molecules interact, that such sites are equivalent in terms of their interaction with adsorbing dye molecules and, also, that there is no interaction between either the sites or between the dye molecules which occupy the sites; furthermore, the occupation of an adsorption site by a dye molecule renders that particular site incapable of interaction with further adsorbed dye molecules. Whilst all of these explicit site and site/adsorbate requirements that are a prerequisite of a Langmuir-type mechanism may well be met in the case of cellulosic substrates and direct dye molecules, given our current lack of understanding of both cellulose structure and the manner of dye-substrate interactions, the precise nature of such dye sites is unclear. Of course, owing to the proliferation of -OH groups in cellulose, it seems likely that the specific sites in cellulose with which direct dye molecules could interact are -

OH groups. However, adherence of direct dye adsorption to a Langmuir-type mechanism implies some form of pronounced selectivity of the interacting -OH groups insofar as, the dye molecules may interact only with a particular type of –OH group or some –OH groups in the fibre may be differently accessible to dye molecules (2). Importantly, a Langmuir-type adsorption mechanism precludes interaction between adsorbed dye molecules present at a specific site within the substrate, which clearly means that dye aggregation cannot play any part in dye-fibre interaction, which appears somewhat surprising, bearing in mind the marked predisposition of direct dyes to self-associate.

Of course, the better correlation observed between experimentally obtained direct dye adsorption data and a Langmuir-type equation does not necessarily mean that the sigmoidal-shaped adsorption curves that are characteristic of direct dye adsorption on cellulosic substrates (eg Figure 6) are not obtained. It simply means that the interactions between the direct dyes and the substrate are specific, which is indicative of homogeneity of adsorption site. This contrasts with the situation that prevails in the case of adherence to a Freundlich-type adsorption mechanism, in that the cellulosic substrate would be heterogeneous and dye-fibre interactions would be diffuse in nature. Essentially, the discrepancies between theoretically derived interpretations of experimentally obtained equilibrium adsorption data reflect the highly complex nature of both dye-dye and dye-electrolyte interactions, as well as the inherent difficulties that attend experimental investigation of the environment that exists within solid textile substrates.

In this context, as mentioned above, in immersion dyeing, all of the constituents of the direct dye/electrolyte/cellulosic fibre system (ie the dye, inorganic electrolyte and fibre) are hydrated and, therefore, during aqueous immersion dyeing, dyebath solution surrounds the fibre and is present in the interstitial volume within the fibrous substrate (ie the volume or space between the constituent polymer macromolecules). The physical state of the dye within the dyebath therefore applies to the whole of the dye/fibre system, including dyebath solution that is present within the substrate in/from which dye diffusion/adsorption occurs. Consequently, the promotion of direct dye aggregation in solution by added electrolyte will permeate all regions of the dye/electrolyte/fibre system, including the dyebath solution that resides within the interstitial regions of the fibre (a detailed account of the concept of interstitial dye solution and its relevance to direct dye adsorption is presented in the following part of the paper). Thus, if dye adsorption proceeds via a Langmuir-type mechanism, the ensuing monolayer of adsorbed dye molecules in the fibre would imply adsorption of monomolecular dye molecules. Furthermore, according to the precepts of the Langmuir-type adsorption mechanism, dye adsorption cannot occur via the formation of multilayers of adsorbed dye molecules, since there can be no interaction between adsorbed dye molecules. Therefore, the adsorption of dye via association with previously adsorbed molecules in the substrate or that of aggregated dye molecules from the dyebath, can play no part in the sorption process.

Thus, Freundlich-type and Langmuir-type adsorption mechanisms differ fundamentally in terms of both their interpretation of the likely contribution of dye aggregation to dye-fibre interaction and, therefore, the role of added electrolyte in direct dyeing. According to the former mechanism, dye aggregation is a likely inherent characteristic of dye-fibre interaction and, therefore, added electrolyte may well expedite such dye-fibre interaction. In contrast, according to a Langmuir-type adsorption mechanism, added inorganic electrolyte is unlikely to influence the way in which direct dyes interact with the cellulosic substrate as dye self-association can play no part in dye-fibre interaction.

In terms of the mechanism of direct dye adsorption, the sizeable, innate differences between the Freundlich-type and Langmuir-type interpretations of experimentally obtained equilibrium direct dye adsorption data can be attributed to the highly complex nature of dye-dye, dye-electrolyte and dye-fibre interactions as well as our general lack of understanding of these important elements of dye sorption.

5.4.2 mathematical models

In this context, because NaCl or Na_2SO_4 is added to direct dyebaths, several mathematical models of direct dye adsorption have been developed over many decades, based on both Freundlich-type and Langmuir-type mechanisms. Such models have also been employed to evaluate the effect of electrolyte on equilibrium adsorption of anionic dyes from wastewater onto various cellulosic adsorbents [eg (102, 103)]. The most widely accepted thermodynamic model of the direct dye/inorganic electrolyte/cellulosic substrate system (2) is that of Marshall and Peters (51). In this particular *diffuse adsorption* model, the dye-fibre system is divided into two parts, namely an external solution phase and an internal solution phase located within the fibre; adsorbed dye anions and electrolyte ions are dissolved in these two phases. The mathematical treatment of this system is complicated because of the need to account for the effect of added inorganic electrolyte on dye equilibrium. In essence, according to this model, in the case of a dye of the form Na_zD^-, the thermodynamic standard affinity of the dye, $-\Delta\mu^\theta$, is expressed in the form of Eq 2, in which the concentration of dye anions, $[D^-]$, and sodium cations, $[Na^+]^z$, in the fibre is quantified on a volume basis (eg g l^{-1} or mol l^{-1}) of internal aqueous phase (an explanation of the consequences of using the same or different units for measuring $[D]_f$ and $[D]_s$ is provided in the Appendix). All of the amounts in Eq 2 are measurable except for $[Na^+]_f$, which must be calculated using Donnan membrane equilibrium theory (2).

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

In general, regardless of the particular thermodynamic model adopted, the agreement between experimentally determined data and theoretically derived isothermal plots is far from ideal, especially when high electrolyte concentrations are employed in dyeing. This divergence between theoretical calculations and experimental observations arise primarily because of the complex nature of direct dye-inorganic electrolyte interactions, which is exacerbated by a diffuse understanding of the precise mechanism by which added electrolyte influences dye-fibre substantivity and, perhaps more significantly, because of the vitally important combinatorial nature of the effects of liquor ratio and added inorganic electrolyte on direct dye uptake. Indeed, the major difficulty encountered in the use of Eq 2 and other related equations, is determining precise values for $[Na^+]_f$, which is complicated because of the need to invoke the concept of (fibre) internal volume (usually expressed in terms of the Volume Term, V, l kg^{-1}) and its mathematical interpretation (2). A further major contributor to the difficulties that are encountered when deriving theoretical equations that adequately fit observed adsorption data stems from the likely prominent role that dye aggregation in solution plays in direct dye uptake (section 5.2) and our imprecise understanding of this phenomenon.

From the foregoing, it follows that if it were possible to dye cellulosic fibres in the absence of added electrolyte then a much simpler thermodynamic treatment of the ensuing, simpler, direct dye/cellulosic fibre dyeing system could be developed that may provide better agreement between theoretical calculations and experimentally determined data. In this context, a subsequent paper will present a thermodynamic model that attempts to rectify the experimental-theoretical discrepancies displayed by current thermodynamic treatments of the direct dye/added electrolyte/cellulosic fibre system, such as that described by Eq 2.

5.5 kinetics of dyeing

Traditionally, the mechanism by which dyeing occurs is interpreted using two approaches namely, studying the dye-fibre system at equilibrium (ie the thermodynamics of dyeing) or before equilibrium is achieved (ie the kinetics of dyeing). In the latter context, because commercial exhaust dyeing processes are rarely carried out to equilibrium, but instead, are designed to provide dyeings within as short a time as possible, the kinetic aspects of dye adsorption have received much attention, since they provide information about the rate at which dyes diffuse within the dyebath and fibre phases.

Briefly, diffusion is the process by which all matter (including dye molecules) transfer within a system from a region of higher concentration to one of lower concentration. Diffusion proceeds in the direction of the concentration gradient that exists between the region of higher concentration and the region of lower concentration. The driving force behind this random molecular motion of individual molecules is the difference in concentration between the two regions.

The diffusional behaviour of direct dyes within cellulosic fibres is commonly described in terms of the pore model of dye diffusion that was devised in the 1930's (104-106) and subsequently developed. In this model, the dye molecules are assumed to diffuse within a network of water-filled, interconnecting pores within the fibre and, at the same time, become adsorbed onto the pore walls. However, debate has attended the precise nature of the diffusional processes that occur within the substrate, in particular the relative contributions of diffusion along pore surfaces and diffusion within pores; essentially, various transport mechanisms have been developed that invoke diffusion along both pores and pore surfaces [(2)].

In terms of the use of inorganic electrolyte to promote the uptake of direct dyes on cellulosic fibres, dye diffusion within such substrates is markedly dependent on added electrolyte [eg (2, 58, 96, 107)], with values of diffusion coefficient decreasing with increasing amount of added electrolyte (108).

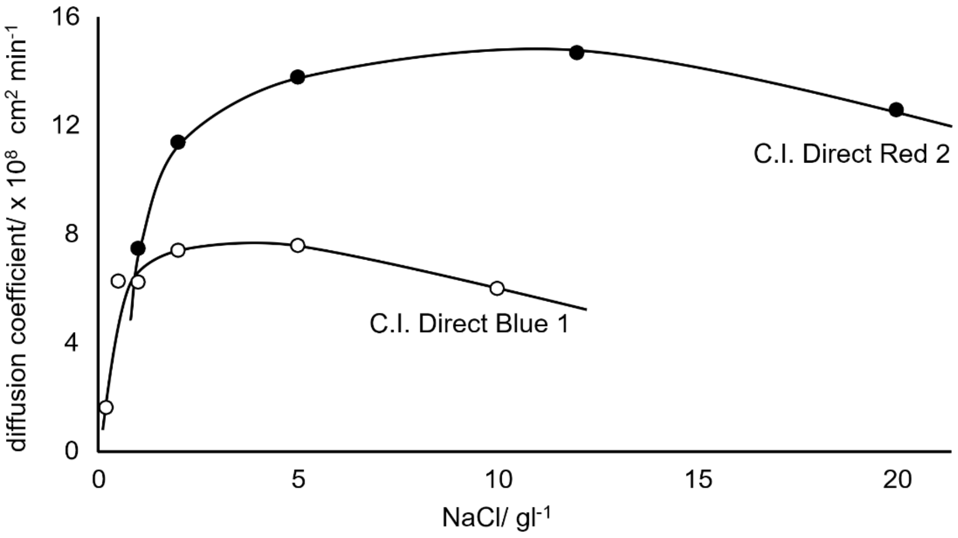


Figure 7 Effect of added NaCl on the diffusion coefficient of C.I. Direct Blue 1 and C.I. Direct Red 2 in CV film; 101°C; 0.05 gl^{-1} dye; plotted using data from (36)

For example, as Figure 7 shows, at low amounts of added inorganic electrolyte, the apparent diffusion coefficients of two purified direct dyes in CV sheet was found to increase rapidly as a function of added electrolyte, which was attributed to the added electrolyte lowering the electrical potential barrier to dye diffusion presented by the negative charge on the fibre surface (36, 108). Thereafter, the apparent diffusion coefficient reached a maximum value and then gradually decreased at higher amounts of added electrolyte (Figure 7). The observed decrease was ascribed to a lower degree of fibre swelling in concentrated electrolyte solution, as well as effects attributable to dye aggregation (108).

Similar curved plots of apparent diffusion coefficient as a function of electrolyte concentration have been secured for various divalent cation salts in the case of purified C.I. Direct Blue 1 and monovalent salts in the case of purified C.I. Direct Red 2 in CV sheet (7). Dye aggregation in solution may also account for the observation that for dyes which display a propensity to aggregate in solution, dye diffusion does not occur from a constant dye concentration at the surface of the substrate (2).

Various models have been used to analyse the kinetics of direct dye removal from wastewater by adsorption onto cellulosic materials, such as the Lagergren pseudo-first-order rate equation, according to which adsorption rate is proportional to the concentration of the diffusing species and is characterised by diffusion through a boundary. Various pseudo-second-order rate equations have also been utilised that assume chemisorption may be the rate-controlling step in the adsorption process [eg see (100, 103, 109-112). Kinetic models have also been employed to describe the effect of electrolyte on the rate of adsorption of anionic dyes from wastewater onto cellulosic materials (102, 103).

Studies, such as those presented above, suggest that added inorganic electrolyte has a marked effect upon the diffusional behaviour of direct dyes in cellulosic fibres. Also, the presence of added electrolyte has a complicating effect on the various models that have been developed to interpret the diffusional behaviour of the dyes. Thus, if it were possible to dye cellulosic fibres in the absence of added electrolyte then this might enable a much simpler interpretation of the ensuing, simpler, direct dye-cellulosic fibre diffusion process; this will be addressed in the subsequent part of this paper.

7 conclusions

Although several theories have been proposed to explain the promotional effect imparted by added inorganic electrolyte on the uptake of direct dyes (and other types of anionic dye) on cellulosic fibres, none of these theories satisfactorily explains the promotional effect of added electrolyte on direct dye uptake in terms of the currently accepted mechanism by which direct dyes are adsorbed on cellulosic fibres.

In the latter context, the mechanism by which dye adsorption has occurred is conventionally construed from mathematical interpretations of isothermal equilibrium dye adsorption data that take the form of complex equations that seek to calculate the thermodynamic standard affinity of direct dyes on cellulosic substrates, $-\Delta\mu^{\theta}$. However, such analysis provides no meaningful information about how dyeing proceeds prior to equilibrium, which is of significance in relation to commercial immersion dyeing processes which are designed to achieve complete dye uptake within a prescribed duration of dyeing. In addition, conventional analysis cannot satisfactorily explain why direct dyes display inherently low substantivity towards cellulosic fibres in the absence of added inorganic electrolyte, nor does it account for the remarkable ability of added inorganic electrolyte to promote dye uptake.

In the latter context, as discussed above, it seems likely that the addition of 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 reduces the solubility of the dye in the dyebath. Unfortunately, whilst such electrolyte-induced dye aggregation offers a reasonable explanation as to how added inorganic electrolyte promotes direct dye uptake, the physical process of electrolyte-induced direct dye self-association in solution and, more importantly, the effect of this aggregation on the solubility of the dye in the dyebath, cannot be explained using the currently accepted physico-chemical models that seek to describe the mechanism by which direct dyes are adsorbed on cellulosic fibres. Thus, an alternative model is required that is able to explain the effects of electrolyte-induced aggregation and consequent reduced dye solubility on direct dye uptake. This is the subject of the next part of this paper.

Appendix

As mentioned, in terms of the mechanism by which direct dyes are adsorbed onto cotton and other cellulosic substrates, the partition of the dye between the fibre and solution phases at the end of equilibrium dyeing is commonly expressed in terms of the thermodynamic standard affinity of the dye, $-\Delta\mu^{\theta}$, which is calculated from equilibrium dye adsorption data, using a mathematical interpretation of Eq 1, such as Eq 2. Typically, the amount of fibre used in dyeing processes is measured as a mass unit (eg kg) and the volume of the dyebath measured in l, from which it follows that the amounts of dye in the fibre and dyebath phases, $[D]_f$ and $[D]_s$ in Eq 1 (and derivatives thereof), will be described in terms of, for example, grams of dye per unit mass of fibre in the case of $[D]_f$ (eg units of $[D]_f$ are g kg^{-1}) and grams of dye per litre of solution for $[D]_s$ (eg units of $[D]_s$ are g l^{-1}). Clearly, as the same units are not employed for $[D]_f$ and $[D]_s$, it follows that the partition constant K has the dimensions of l kg^{-1} (Eq A1) whereas when employed in equations such as Eq 2, K should be dimensionless.

$$K = \frac{[D]_\mathrm{f}}{[D]_\mathrm{s}} = \frac{\mathrm{g\ kg^{-1}}}{\mathrm{g\ l^{-1}}} = \mathrm{l\ kg^{-1}} \qquad \mathrm{A1}$$

One way to resolve this issue is to express the volume of the dyebath, *$[D]_s$*, in mass terms (eg g kg^{-1}) rather than volume terms (eg g l^{-1}), and the problem of dimensions is removed with the addition of only a small error.

However, an alternative approach, which is often utilised in the case of the thermodynamics of adsorption of ionic dyes on ionic fibres (2, 96, 98), presumes that the fibre phase contains a liquid of *volume*, *V* l kg^{-1} within which the adsorbed dye molecules reside. Accordingly, Eq 1 is modified by the inclusion of a *Volume term*, *V* (Eq A2) so that the equilibrium partition coefficient, *K* is dimensionless.

$$K = \frac{[D]_\mathrm{f}}{\mathrm{V}[D]_s} = \frac{\mathrm{g\ kg^{-1}}}{\mathrm{l\ kg^{-1}\ .\ g\ l^{-1}}} \qquad \mathrm{A2}$$

Unfortunately, the precise nature of the volume term *V*, which was first employed by Neale *et al* (35), is not entirely understood, being regarded as either a constant factor that applies to a particular type of cellulosic fibre or an arbitrary value (2).

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