Received: 4 September 2020 | Revised: 8 March 2021 | Accepted: 9 March 2021

DOI: 10.1111/cote.12547

REVIEW ARTICLE

Coloration Technology

The role of inorganic electrolyte (salt) in cellulosic fibre dyeing: Part 1 fundamental aspects

Stephen M Burkinshaw

University of Leeds, Leeds, UK

Correspondence
Stephen M Burkinshaw, University of Leeds, Leeds, LS2 9JT, UK.
Email: s.m.burkinshaw@leeds.ac.uk

Abstract

This review concerns the application of dyes to both natural and man-made cellulosic fibres from aqueous dyebaths using exhaust dyeing processes and the role of added inorganic electrolyte in such dyeing systems. This part of the article presents a review of the fundamental properties and characteristics of cellulosic fibres and each of the five classes of dye employed for their coloration, as well as the essential principles involved in the application of the various types of dye to cellulosic fibres. In the next part of the article, the various theories and concepts which have been proposed to account for the promotional effect exerted by added inorganic electrolyte on dye uptake are reviewed and scrutinised, from the viewpoints of the essential physicochemical properties of the five classes of dye that are used and the fundamental aspects of their application.

1 | INTRODUCTION

Despite the widespread global popularity of both natural and man-made cellulosic fibres, the immersion application of each of the five classes of dye used for their coloration, namely vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes, is intrinsically flawed on environmental grounds because inorganic electrolyte, commonly in the form of sodium chloride (NaCl) or sodium sulphate (Na_2SO_4), must be added to the aqueous dyebath in order to promote dye uptake and ensure that acceptable depths of shade are secured. The impressive promotional ability of inorganic electrolyte is illustrated by the results presented in Figure 1.

Whilst the amount of added inorganic electrolyte employed in exhaust dyeing processes varies according to several process variables, such as the class of dye, type of cellulosic fibre, liquor ratio, dyeing machine, etc., the ostensibly indispensable usage of NaCl or Na_2SO_4 in cellulosic fibre dyeing, which can be of the order of 1 kg of electrolyte per kilogram of cellulosic fibre dyed, contributes significantly to the overall expense of dyeing, not only in terms of the direct cost of the added electrolyte used but, more disturbingly, because of the considerably much larger indirect costs of the rigorous treatment and disposal protocols that must be employed to remediate the highly saline residual dyeing wastewater (see for example[3-9] and the references cited therein). In the latter context, an appreciation of the magnitude of both the financial and environmental impact posed by the habitual use of inorganic electrolyte in cellulosic fibre dyeing is provided by the severe difficulties experienced by the Tirupur (India) weft knit cotton industry which resulted in the compulsory adoption of zero liquid discharge (ZLD) dyeing processes (see for example[10-18]).

In view of the worldwide prominence of natural and man-made cellulosic fibres and the fundamentally important role of added inorganic electrolyte in the dyeing of cellulosic fibres using vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes, it is to be expected that the mechanism by which NaCl or Na_2SO_4 promotes the uptake of has been the subject of considerable investigation. Whilst this is indeed the case, and many theories/hypotheses/concepts have been proposed, over many decades, to explain this highly complex phenomenon, our understanding of the precise manner by which added inorganic electrolyte promotes dye uptake on cellulosic fibres nevertheless leaves much to be desired.

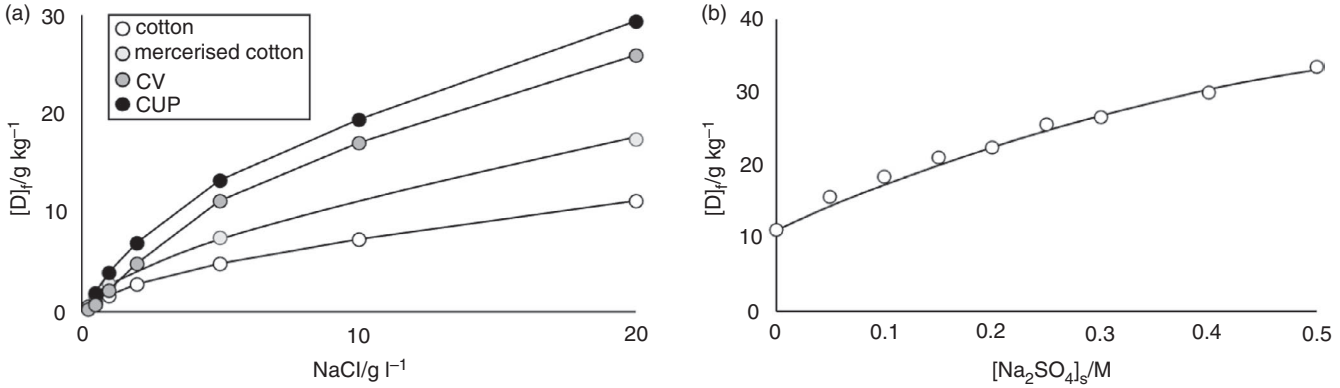


FIGURE 1 Promotional effect of (a) NaCl on uptake of 0.05 g l^{-1} CI Direct Blue 1 on various types of cellulosic fibre (CV, viscose; CUP, cuprammonium rayon) at 90°C; (b) Na_2SO_4 on uptake of 0.065 g l^{-1} CI Vat Green 1 on cotton at 45°C; drawn using data from (a)[1] and (b)[2]

In essence (see[19] and the references cited therein), the ambiguity that pervades our understanding of the role of inorganic electrolyte in cellulosic fibre dyeing is the corollary of several, fundamentally important, but, in most cases, not entirely resolved, concepts, namely:

- the complex, extensively H-bonded, three-dimensional structure of liquid water and the influence of electrolyte ions on water structure;
- the multifaceted nature of dye–water interactions, which includes theories of aqueous dye solubility and dye self-association;
- the effects of electrolyte ions on both the aqueous solubility and aggregation behaviour of anionic dyes/anionic dye precursors (herein the term *dye precursor* relates to azoic coupling components, as discussed in Section 2.4.3) in multi-component, aqueous, ionic dyebath systems;
- the fine structure of both natural and man-made cellulosic fibres and that of the constituent cellulose macromolecule;
- the complex nature of water–fibre and water–cellulose interactions;
- the influence of electrolyte ions on cellulose polymer structure, and;
- the intricate, highly complex and multifarious areas of dye–cellulose polymer and dye–cellulosic fibre interactions.

Whilst this review article does not make any attempt to provide detailed accounts of the diverse, intrinsically highly complicated concepts listed above, appropriate aspects of these fundamentally important topics are discussed in the hope that this will provide useful background information relevant to the various theories and hypotheses which have been proposed to account for the promotional effect of added NaCl or Na_2SO_4 on the uptake of anionic dyes and, also, help explain why the *anionic dye/dye precursor-cellulosic fibre* dyeing system is so profoundly complex and perplexing.

Furthermore, as various types of cellulosic fibre are available and the five classes of dye employed for their coloration are applied using diverse exhaust application conditions (eg pH, temperature, dyeing auxiliaries, etc.), display differing adsorption behaviour and also furnish dyeings of varying characteristic properties (eg brightness, cost, fastness, etc.), the likely contribution of the various fundamental concepts listed earlier to the phenomenon of inorganic electrolyte-induced dye uptake promotion, can only be fully appreciated by considering their correlation with the fundamental aspects of the aqueous cellulosic fibre dyeing system.

Because the dyeing of cellulosic fibres using vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes is a large, multi-component system in which the role of inorganic electrolyte in dyeing has manifold likely interpretations, it was decided that in view of the large amount of information involved, this article would benefit from being presented in two parts.

This part of the article presents a review of the fundamental structure and properties of cellulosic fibres, as well as the essential physico-chemical properties of vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes, together with the various application conditions that are commonly utilised for each of the five classes of dye. The complex and multifaceted role of water in the aqueous cellulosic fibre dyeing system is examined from the viewpoints of the sorption of this unique solvent by cellulosic fibres and its consequences for aqueous dyeing, namely water-induced fibre swelling and fibre plasticisation, as well as the often overlooked but profoundly important role of liquor ratio in cellulosic fibre dyeing.

The second part of the article presents a detailed review and critical analysis of the various theories/hypotheses/concepts which have been proposed to account for the promotional effect exerted by added inorganic electrolyte on the uptake of vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes. As a corollary of this review/analysis exercise, a simple theoretical model is described which seeks to explain how added NaCl or Na_2SO_4 promotes uptake of each of the five dye classes on cellulosic fibres.

2 | THE CELLULOSIC FIBRE DYEING SYSTEM

The four most important components of aqueous cellulosic dyeing processes are:

1. Water
2. Cellulosic fibre
3. Vat dye, sulphur dye, azoic colourant (coupling component and diazo component), direct dye or reactive dye
4. Inorganic electrolyte

It therefore seems pertinent to review the fundamental aspects of these four system components in terms of their relevance to the likely role of inorganic electrolyte in cellulosic fibre dyeing.

2.1 | Water

Whilst it seems reasonable that a discussion of both the structure and properties of water would be germane, it is neither appropriate, nor possible, within the confines of this review, to undertake such an exploration of this extremely large and complicated topic. Instead, the reader is directed to comprehensive accounts[20-28] of both the unique physical structure of water in each of its four physical forms (solid, liquid, vapour and supercritical fluid) and the plethora of water structure models that have been proposed over many years, as well as the ways in which the extensive, co-operative, H-bonded water structure is responsible for the unique and widely-known *anomalous behaviour* of water's macroscopic physical and chemical properties (eg T_m, T_b, pK_a, etc.).

For an introduction to the role of water in aqueous dyeing processes see[19,29,30] and the references cited therein; general accounts of textile fibre–water and polymer–water interactions, as well as the various theories and models that have been proposed to describe the complex and varied ways in which water molecules and fibre/polymer molecules interact, are available.[19,31-36]

By way of brief background, although water is of course a critically important component of all aqueous dyeing processes, in so far as this unique solvent undertakes manifold dyebath functions that are of essentially mechanical/thermal/chemical nature (eg fibre transportation, fibre swelling, heating, cooling, pH control, dye dissolution, etc.), detailed accounts of the use of water in dyeing are surprisingly rare (see[19] and the references cited therein). The effects that water exert on cellulosic fibres can be expected to vary widely, from those which occur at a molecular level (eg sorption onto hydroxyl, -OH, groups located on cellulose polymer chains that reside within the amorphous regions of the semi-crystalline fibre) to those which are of essentially mechanical origin

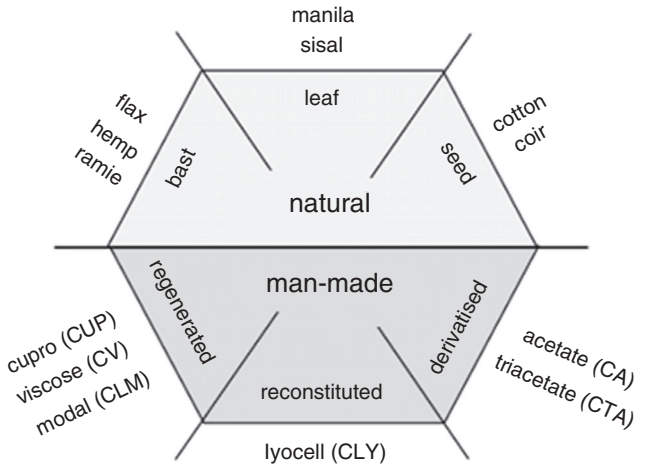


FIGURE 2 Classification of cellulosic fibres

(eg fibre swelling, fibre plasticisation); likewise, the roles of water in for example, dye solvation and dye self-association, are each highly complicated, multifaceted phenomena.

The amount of water used in an aqueous exhaust dyeing process, as commonly articulated in terms of *liquor ratio*, which has a profound effect on both the progress (eg rate of dyeing, extent of dye uptake, etc.) and outcome (eg uniformity of dyeing, etc.) of the coloration process. Any discussion of the possible role of added inorganic electrolyte in immersion cellulosic fibre dyeing must necessarily involve the influence of dissolved electrolyte ions on the structure and properties of liquid water, as well as the influence of NaCl or Na_2SO_4 on the solvency of dye/dye precursor anions, the fine structure of the fibre macromolecule, etc.

Whilst some of these water-related phenomena are considered later, the topics of electrolyte–water, electrolyte–dye and electrolyte–fibre interactions are discussed in the second part of the article as these form the bases of the various theories/hypotheses/concepts that have been proposed to account for the role of added inorganic electrolyte in cellulosic fibre dyeing.

2.2 | Cellulosic fibres

The following account provides only a brief introduction to the essential features of the chemistry, structure and properties of the various common types of cellulosic fibre in relation to their coloration; for detailed accounts see for example[19,37-41]

Several types of cellulosic fibre are available (Figure 2), namely, natural cellulosic fibres of either bast, leaf or seed derivation, as well as various types of *man-made cellulosic fibre*, including *regenerated cellulosic fibres*, *reconstituted cellulosic fibres* and *derivatised cellulosic fibres*.[19,42] The bracketed terms in Figure 2 denote the appropriate abbreviation allocated by BISFA (Bureau International pour la

Standardisation des Fibres Artificielles)[43] to man-made fibres, as exemplified by viscose (CV), acetate (CA), etc.

2.2.1 | Usage

Cellulosic fibres enjoy considerable usage, as illustrated by the fact that in 2017, a total of ~31 × 10^6 T of natural and man-made cellulosic fibres were produced globally, with cotton accounting for ~27% and its man-made counterparts ~6%, respectively, of the 94.8.1 × 10^6 T of world textile fibre production[44] (Figure 3).

Although 100% cellulosic textile materials are widespread, cellulosic fibres also enjoy considerable usage in admixture with other types of fibre, as exemplified by the most widely used of all textile blend materials, *polycotton*, in which cotton is blended with between ~30% to 70% of the world's most popular textile fibre, poly(ethylene terephthalate) (PET) (Figure 3).

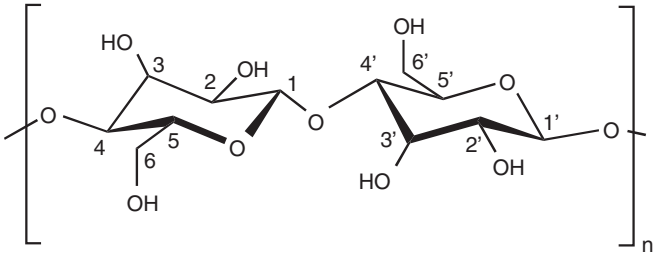
As global textile fibre demand can only be expected to increase in the foreseeable future, in-line with increases in world population and global economic prosperity, so the respective levels of global fibre production and popularity presented in Figure 3 can be expected to increase ad interim.

Because of the outstanding popularity of cotton, studies relating to cellulosic fibre dyeing are dominated by this particular type of natural cellulosic fibre: nonetheless, the underlying fundamental findings of such studies can be considered to apply, generally, to other types of natural cellulosic fibres (eg ramie, flax, etc.) as well as both regenerated and reconstituted cellulosic fibres (eg CV, CLY etc.).

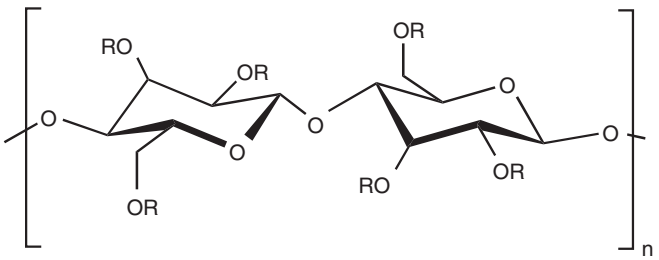
2.2.2 | Chemistry and fine structure

The structure, morphology and properties of natural, regenerated, reconstituted and derivatised cellulosic fibres have received considerable attention, as has that of the constituent polymer, *cellulose* [45-55]; as such, the following serves only as a brief introduction/reconsideration.

The term cellulosic fibre indicates that each of the natural and man-made cellulosic fibres illustrated in Figure 2 comprises the linear polymer cellulose, **I**, in which *β*-D(+)-glucopyranose monomers are linked together via 1,4-glycosidic bonds between the -OH groups at the C-1 position of one glucose molecule and the C-4 position of another. Each monomer, or *anhydroglucose unit* (AGU), contains one primary -OH group at C-6 and two secondary -OH groups at C-2 and C-3, respectively; the structural unit shown below for cellulose, **I**, is often referred to as *cellobiose*, a dissacharide that comprises two AGUs.



I



II

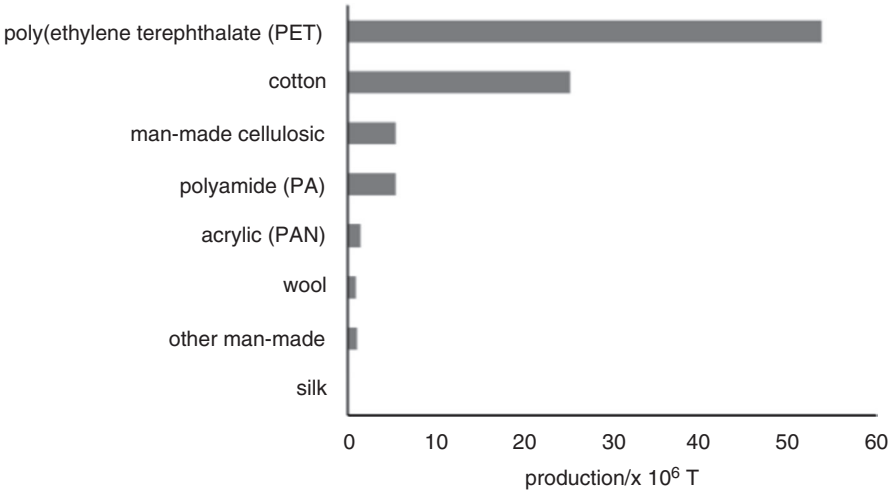
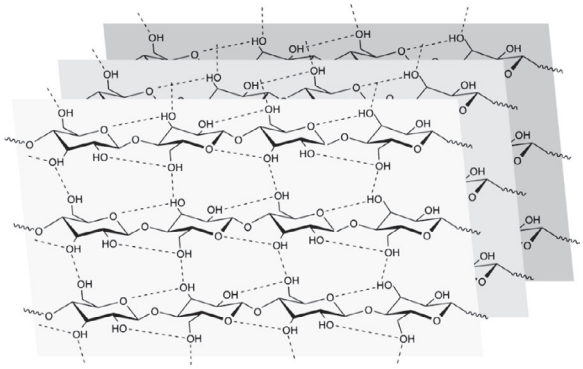


FIGURE 3 World textile fibre production in 2017; drawn using data from[44]

The cellulose polymer, **I**, that is present in both regenerated and reconstituted cellulosic fibres (eg CLY, CV, etc.) is indistinguishable from that of their natural cellulosic fibre counterparts (eg cotton, flax, etc.), even though distinctly different processing conditions will have been utilised for their production (eg natural cellulosic fibres: cultivation of naturally occurring sources of cellulose; man-made cellulosic fibres: manufacture from naturally occurring sources of cellulose). However, as the polymers utilised in both CA and CTA are derivatives of cellulose (ie esters of different degrees of substitution, **II**: CA 66–84% R = -OH, ~26–34% R = $-OCH_3$; CTA 100% R = $-OCH_3$), the two derivatised cellulosic fibres differ appreciably from their regenerated and reconstituted cellulosic fibre counterparts, including, from the viewpoint of this review, dyeability, insofar as CA and CTA fibres are dyed almost exclusively using disperse dyes. As such, this review does not concern either of the two derivatised cellulosic fibres, CA and CTA, the reader being directed elsewhere for accounts of the properties and dyeability of these two fibre types.[19,50,52,56-62]

The abundant number of hydroxyl groups in the cellulose polymer, **I**, that makes up all natural cellulosic fibres (eg cotton, ramie, etc.) as well as regenerated and reconstituted cellulosic fibres (eg CV, CLY, etc.), enables both *intramolecular* H-bonding to occur between the -OH groups in each glucose ring with -OH groups in the same chain molecule [O(3)-H···O(5) and O(2)-H···O(6)), as well as *intermolecular* H-bonding between -OH groups in neighbouring macromolecular chains [O(6)-H···O(3)], as shown by the dotted lines in **III**. As H-bonding occurs in only one plane,[32] a unique, extensively H-bonded, three-dimensional macromolecular structure is formed, in which sheets of H-bonded cellulose polymer chains associate laterally, via numerous inter-sheet C–H···O hydrogen bonds and van der Waals interactions [eg[51,63-68]], as illustrated by the simplified structure presented in **III**.



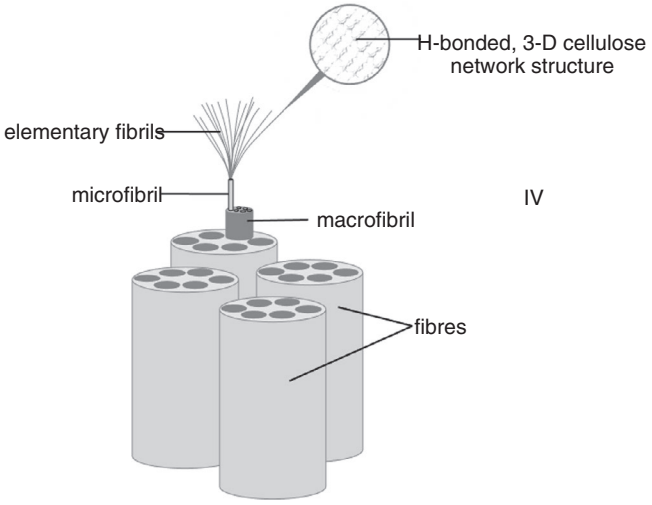
III

Despite the overwhelming predominance of -OH groups, the cellulose macromolecule also contains a comparatively much smaller number of hydrophilic carboxyl (-COOH) groups (eg -COOH content of cotton 0.006 mol l^{-1} [69]; -OH content of cotton 11.22 mol l^{-1} [70]), which arise due to partial oxidation processes, notably bleaching, encountered during fibre production.[19,71-74] Although the carboxyl group content varies for different types of cellulosic fibres and substrates (eg -COOH content/ mol kg^{-1}: mercerised cotton 0.01-0.02; regenerated cellulose 0.01-0.05[75]; CV: 0.025[76]; cellophane: 0.05[77]; CLY 0.021; 0.049[78]) the presence of even such relatively small amounts of ionised carboxyl groups within cellulosic fibres is of significance with regards both water sorption behaviour (Section 2.2.3) and, more significantly, from the viewpoint of this review, the likely mechanism by which added inorganic electrolyte promotes the uptake of anionic dyes on cellulosic fibres: the potential role of $-COO^-$ groups in cellulosic fibre dyeing is discussed in the second part of the article.

The ensuing, extensively H-bonded, three-dimensional structure of the cellulose macromolecule facilitates the *self-association* of the composite macromolecular chains which results in the formation of highly ordered regions that likely comprise *crystallites*, as well as regions of lower order referred to as *amorphous domains*. Consequently, all natural and man-made cellulosic fibres are *semi-crystalline* materials, despite the fact that different manufacturing routes will have been utilised in their production. In the context of the crystallinity of natural, regenerated and reconstituted cellulosic fibres, the *degree of crystallinity* varies widely (eg typical degree of crystallinity: cotton 60-70%; CV 40%; CLY 60%[32,48,79,80]), several crystal forms having been identified that vary structurally owing to differences in both intramolecular and intermolecular H-bonding within the various crystal forms[39,51,63,81-87]:

- Cellulose I: the natural allomorph present in cotton, ramie, etc. which is dimorphic, in that two crystalline variants arise namely Cellulose Iα and Cellulose Iβ;
- Cellulose II: obtained when Cellulose I is regenerated as exemplified by CV, or treated with high concentrations of alkali as in the case of mercerised cotton;
- Cellulose III, Cellulose III_1 and Cellulose III_2, Cellulose IV, Cellulose IV_1 and Cellulose IV_2 as well as Cellulose IX: less common crystal forms that arise by virtue of specific treatments of cellulose allomorphs.

The *fine structure* of cellulosic fibres, especially that of cotton, has received considerable attention. For example, cotton is considered to comprise crystalline *macrofibrils* which consist of smaller *microfibrils* that are made up of *elementary fibrils* which contain several AGUs, as represented by the simplified hierarchical microfibrillar structure depicted in **IV**. Whereas CV fibres can be described by the *fringed micelle model* and CML fibres defined in terms of the *fringed fibril model*, in contrast, a *paracrystalline* structure has been proposed for CLY fibres (see[19,48,88,89] for discussions).



The unique, H-bonded, three-dimensional network structure of cellulose polymers, which stems from the combination of the interchain, intrachain and inter-sheet interactions discussed above, is responsible for the characteristic chemical and physical properties displayed by both natural and man-made cellulosic fibre materials (eg hydrophilicity, strength, absorbency, etc.). As these properties include water sorption, swelling and plasticisation, which are of crucial importance from the viewpoint of aqueous dyeing processes, they merit brief consideration.

2.2.3 | Water sorption

The characteristic *hygroscopic* nature of cellulosic fibres accrues primarily from the presence of -OH groups located on polymer chains that reside within the amorphous domains of the substrate, with which water molecules can interact via H-bonding. However, for various structural reasons[19,47,90-92] not all of the component hydroxyl groups within cellulose polymers are equally accessible towards water molecules and, therefore, towards other types of molecule that are dissolved/dispersed within the water, namely dye molecules, NaCl, Na_2SO_4, etc. In addition, the constituent hydroxyl groups do not display equivalent levels of reactivity, which, in the case of cotton, follows the order: OH-3 << OH-6 < OH-2.

Hydrogen bonding can also be expected to occur between water molecules and the small number of carboxyl groups present in the cellulose polymer.[19]

The extent of water sorption varies for different types of cellulosic fibre (Table 1) owing to various fine structure variations which are commonly quantified in terms of the *degree of polymerisation* (DP), *crystallinity index* (CI), *orientation factor* (*f*), etc., of the material.

The sorption of water moisture by cellulose materials is considered to occur via two simultaneous processes namely, H-bond interactions at accessible -OH groups located within the amorphous domains and on surfaces of elementary fibrils and crystal surfaces at *relative humidity* (RH) < 50-60%, and, at higher values of RH, physical sorption by means of capillary condensation, as well as the formation of multi-layers of water molecules located at the fibre surface or as a result of swelling-induced increased surface area[47]; see[19,32,36,47,94,95] for detailed discussions.

Several models have been proposed to interpret the sorption of water by cellulosic fibres[19,32,36,94,95] of which the most famous is the two-phase model described by Peirce in 1929,[96] that introduced the concept of *directly* and *indirectly sorbed* water molecules which continues to be a feature of contemporary views of water sorption within cellulosic fibres.

2.2.4 | Water-induced swelling

As both natural and man-made cellulosic fibres are able to adsorb water and temporarily retain the sorbed moisture/liquid water, so the volume of the substrate increases, which is accompanied by *anisotropic* swelling (ie lateral swelling > longitudinal swelling), as illustrated by the values of lateral swelling presented in Table 1.

The extent of *water-induced swelling* that cellulosic fibres undergo, which is a consequence of water sorption having disturbed the H-bonded network structure of the cellulose macromolecules and varies for different types of substrate (Table 1), is referred to as *intercrystalline swelling*.[19,32,97] Cellulosic materials are also able to undergo *intracrystalline swelling* when immersed in aqueous solutions of various compounds, as exemplified by sodium hydroxide (NaOH) which is employed in the mercerisation process that is used to modify the physical and chemical properties (including dyeability) of cellulosic fibres.[19,32,54,98]

Because an aqueous dyebath contains dissolved dye ions/dispersed dye molecules, it follows that when water

TABLE 1 Moisture regain and swelling (at 65% Relative Humidity [RH] and 20°C) of some regenerated and reconstituted cellulosic fibres[93]

Fibre	DP/ %	CI/ %	Density/ g cm^{-3}	$f_{\Delta n}$	dtex	Diameter/ µm	Moisture regain/ %	Lateral swelling/ %
CV	235	0.25	1.5045	0.58	1.88	14.3	15.1	36.3
CLY	507	0.37	1.5141	0.69	1.78	14.2	14.6	22.0
CLM	642	0.44	1.5205	0.44	1.82	12.8	14.1	17.4

TABLE 2 Saturation moisture regain (ie moisture uptake at 100% relative humidity) and water-induced plasticisation of some cellulosic fibres[104-110]

Fibre/polymer	Saturation moisture regain/ %	Dry T_g/ °C	Wet T_g/ °C	ΔT_g/ °C
Cotton	22.6 @ 25°C	220–230	<20	~210
CV	33.6 @ 25°C	~180	~60	~120
CTA	11.8 @ 22°C	~180	~90	~90

molecules are sorbed by a cellulosic fibre via association with -OH groups located on polymer chains within the amorphous domains of the substrate, the dissolved/dispersed dye ions/dye molecules accompany the sorbed water molecules and, therefore, occupy the amorphous regions of the water-swollen fibre, being able to interact with appropriate adsorption sites within the macromolecule (most likely -OH groups) and thereby become adsorbed. Water sorption and consequential water-induced swelling are, therefore, necessary pre-requisites for successful aqueous dyeing.

2.2.5 | Water-induced plasticisation

The swelling of cellulosic fibres imparted by sorbed water molecules is accompanied by changes in other physical properties of the substrate, such as rigidity, elasticity, etc., which influence dyeability. Essentially, when sorbed water molecules disturb the extensive, H-bonded structure of the cellulose polymer within the non-crystalline regions of the fibre, which is manifest as water-induced swelling, the water molecules function as *plasticisers*[99-103] (see[19] and references cited therein). As a result of water sorption, cellulosic fibres, therefore, undergo *water-induced plasticisation*, to an extent which can be quantified in terms of the depression in the glass transition temperature (T_g), of the substrate, via the parameter ΔT_g, which simply expresses the difference between the values recorded for the dry T_g (ie the T_g of the fibre when dry) and the wet T_g (ie the T_g of the fibre when wet),[19] as illustrated by the data presented in Table 2.

In general, values of dry T_g reported for cellulosic materials vary according to the particular type and physical form of the cellulose polymer studied as well as the method of thermal analysis utilised (eg dry T_g: *ball milled cellulose* 205°C; *amorphous cellulose* 227°C; *unbleached spruce kraft pulp* 235°C [111]; cotton ~200°C *modulus and stress decay*[112]; cotton 240°C *modulus and resiliency*[113]) in a similar vein, values of wet T_g also vary for different types of cellulosic fibre as shown by the data presented in Table 2.

The characteristically high values of dry T_g (Table 2) reflect the inherently high strength of the H-bonded cellulose network structure. Intriguingly, this three-dimensional network structure is also responsible for the remarkable and sizeable plasticising effect which sorbed water molecules can exert upon cellulosic materials in so far as, the interactions of sorbed water molecules with -OH groups in the polymer chains causes major disruption of the extensively H-bonded cellulose polymer structure, which, as Table 2 shows, corresponds to ΔT_g changes that range between ~90°C and ~210°C. Indeed, the remarkable plasticising effect of sorbed water has been observed for several types of cellulosic material, with values of wet T_g ranging from 0°C to −45°C.[99,102,113]

Thus, when, for example, dry cotton fibres are immersed in an aqueous medium, such as an exhaust dyebath, the intrinsic hydrophilic nature of the cellulose polymer results in the immediate sorption of the order of 22.6% by mass of water which induces fibre swelling that is also accompanied by a significant depression of the substrate's dry T_g which can be of the order of ~200°C (Table 2). The amount of water sorbed will vary according to the type of cellulosic fibre involved, as shown by the values of saturation moisture regain presented in Table 2. Such marked changes in the physical characteristics of the cellulosic material are manifest as a substantial decrease in fibre stiffness and an equally sizeable increase in fibre plasticity. Indeed, the sizeable changes in the physical nature of cellulosic fibres that occur at or about the wet T_g of the substrate are critically important from an aqueous dyeing viewpoint, as the water-swollen, water-plasticised nature of the substrate expedites dye sorption, dye levelling, dye migration, etc.

2.2.6 | Dyeability

For accounts of the dyeing of cellulosic fibres using vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes, see for example.[19,37,61,114-124]

Although the precise nature of the intrinsic *substantivity* (see Section 2.3) displayed towards cellulosic fibres by vat dyes and sulphur dyes, in the form of their respective *leuco derivative* (see Section 2.4.1), azoic colourants in the guise of the contributory azoic coupling component, direct dyes and reactive dyes, has not been unequivocally resolved, it is generally considered[19] that dye–fibre substantivity arises primarily by a combination of H-bonding and van der Waals interactions between appropriate groups in the dye molecules (eg -OH, -NH_2, NH, -COOH, etc.) and accessible hydroxyl groups present in the component macromolecular chains located within the water-swollen amorphous regions of the semi-crystalline fibrous polymer. However, it is of course likely that other forces of interaction, such as dipole–dipole forces, hydrophobic interaction, etc., will contribute to dye–fibre substantivity.[19] In the case of reactive dyes, the presence of a *reactive system* within the dye molecule confers upon the dye molecule the unique ability to form a covalent bond with nucleophilic, *ionised*

hydroxyl groups in the cellulosic substrate (-O^-, which often are denoted as Cell-O^-) under appropriate alkaline conditions; dye–fibre covalent reaction can be considered to contribute towards reactive dye–cellulosic fibre substantivity.[19,125]

As discussed in detail in the next part of the article, the aqueous dyeability of natural and man-made cellulosic fibres using vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes is dominated by water, through a combination of water–cellulose polymer interactions and the related structural modifications which sorbed water impart to the component cellulose macromolecules, as well as, more importantly, the aqueous solubility of the particular class of dye used. Indeed, as also described in the second part of the article, for all exhaust dyeing processes utilised for cellulosic fibres, the solubility of the particular dye/dye precursor anion in the aqueous dyebath under the particular application conditions employed (eg pH, temperature, salinity, alkalinity, etc.) is of crucial importance in terms of not only why inorganic electrolyte is utilised in dyeing but, also, how much NaCl or Na_2SO_4, is added to the vat dye, reactive dye, sulphur dye, etc., aqueous dyebath.

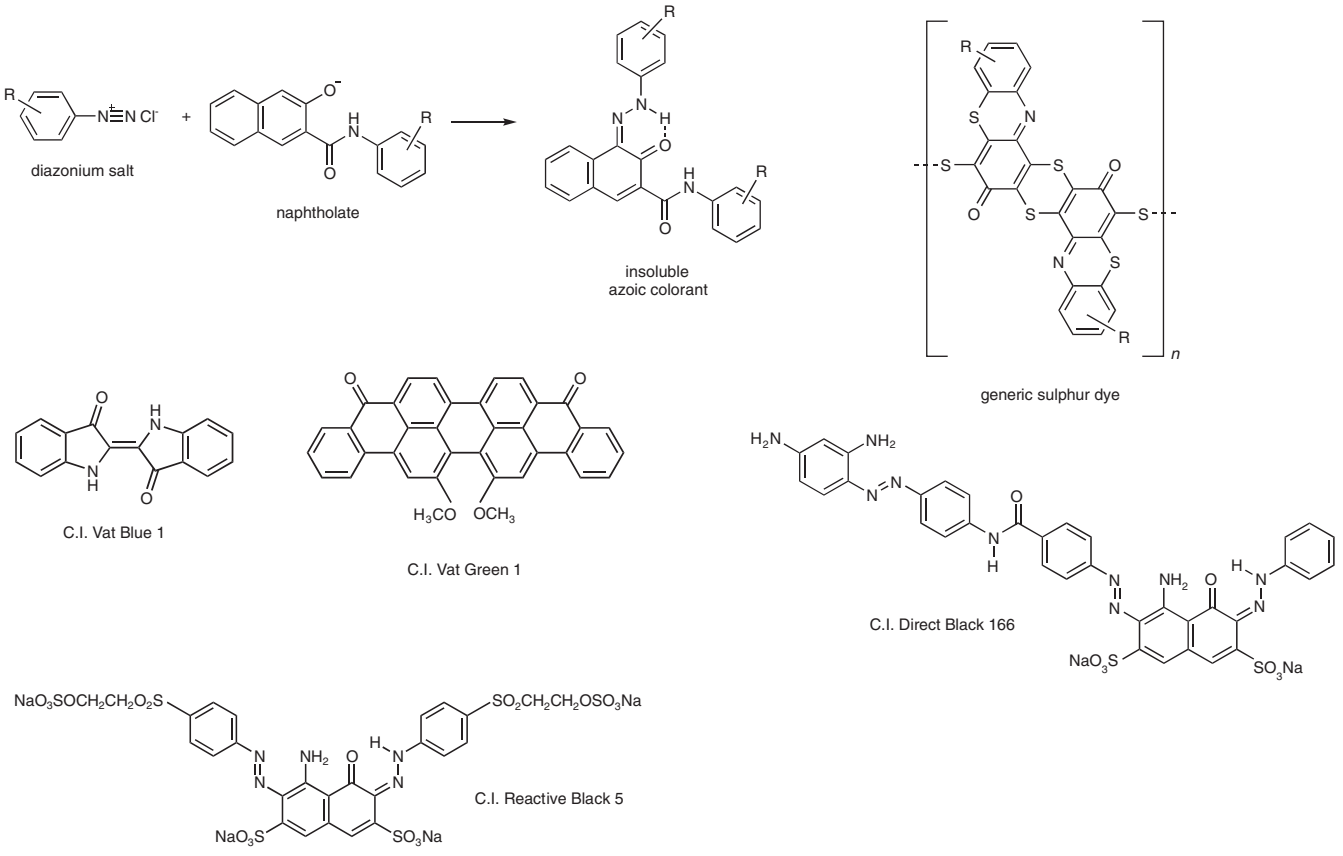
2.3 | Dye classes

As recounted, cellulosic fibres can be dyed using five classes of dye, structural examples of which are shown here.

For the purposes of this review the following definitions are considered to apply:

1. Vat dye: a water-insoluble dye, usually containing keto groups, which is normally applied to the fibre from an alkaline aqueous solution of the reduced enol (leuco) form, which is subsequently oxidised in the fibre to the insoluble form.[126]
2. Sulphur dye: contains sulphur both as an integral part of the chromophore and in attached polysulphide chains, normally applied in the alkali-soluble reduced (leuco) form from a sodium sulphide solution and subsequently oxidised to the insoluble form in the fibre.[126]
3. Azoic colourant: an insoluble azo compound that is formed *in situ* within the cellulosic fibre by the reaction between an azoic diazo component and an azoic coupling component.[19]
4. Direct dye: an anionic dye having substantivity for cellulosic fibres, normally applied from an aqueous dyebath containing an electrolyte.[126]
5. Reactive dye: a dye that under suitable conditions, is capable of reacting chemically with a substrate to form a covalent dye-substrate linkage.[126]

The diverse range of dye classes available for cotton and other types of cellulosic fibre is historical. Whilst the use of vat dyes obtained from natural sources such as plants,



insects, etc., as exemplified by *Tyrian Purple* and *Turkey Red*, has been practiced for several thousand years, the remaining four dye classes were developed in much more recent times, as a consequence of a general increase in scientific investigation and understanding during the eighteenth century and the nineteenth century that culminated in Perkin's serendipitous discovery of *Aniline Purple i*n 1856 and the associated advances in commercial-scale organic synthesis that were required to manufacture this most famous of synthetic dyes.[19,127-129] Indeed, the commercial success of Perkin's outstanding discovery stimulated enormous interest in both the synthesis and commercial production of many types of synthetic dye, including those of relevance to cotton and other types of cellulosic fibres, such as, for example, azoic colourants (1880), the first sulphur dye *Cachou de Laval* (1883), the first direct dye *Congo Red* (CI Direct Red 28; 1884), the first synthetic anthraquininoid vat dye *Indanthren Blue RS* (CI Vat Blue 4; 1901) and, in 1956, the currently most popular of all types of dye utilised on cellulosic fibres, reactive dyes.

Such remarkable developments in dye chemistry resulted in colourants that offered novel and/or enhanced colour gamut, displayed improved fastness to light, laundering, etc., on cotton and the types of man-made cellulosic fibre at the time then available, and were accompanied by parallel developments in dyeing processes that sought to reduce costs, increase productivity, etc. For example, up until the latter part of the nineteenth century, the cellulosic fibres existing at the time could be dyed only using complicated and time-consuming processes that utilised a limited number of dyes, commonly in conjunction with a mordant, typically a metal salt. However, in 1883, Böttiger realised that a novel, red azo dye could be applied to cotton directly in the presence of added inorganic electrolyte (NaCl) without the need for a mordant; the ensuing commercial dye, *Congo Red* (CI Direct Red 28), became the first member of the dye class in the *Colour Index*[130] known as direct dyes. The subsequent, incredibly significant commercial success that attended the introduction of reactive dyes for cellulosic fibres in 1956 was the result of equally innovative advances in application technology, namely a desired level of dyebath alkalinity in combination with a large amount of added NaCl or Na_2SO_4.

2.3.1 | Usage

The commercial introduction of direct dyes in the late nineteenth century and the associated much simpler and shorter dyeing process that did not require recourse to a mordant, proved very popular and direct dyes quickly became the favoured choice for dyeing cotton and other cellulosic fibres. Conversely, the sizeable popularity of direct dyes began to decline in the late 1950s owing to the introduction of reactive dyes that were developed specifically to overcome the inherent inadequacies of direct dyes, namely, their characteristically low/moderate fastness to washing and other wet treatments on cellulosic fibres. Essentially, whereas direct dyes are merely retained physically within the dyed cellulosic substrate at the end of dyeing and consequently typically exhibit only low/moderate levels of wet fastness, reactive dyes are covalently attached to the fibre at the end of dyeing and, therefore, display characteristically excellent levels of wet fastness.

Indeed, since their commercial introduction some 60 or so years ago, the global popularity of reactive dyes has increased steadily to the detriment of not only direct dyes, but also that of the other three classes of dye that can be used on these types of fibre, namely azoic colourants, sulphur dyes and vat dyes, this being reflected in the fact that reactive dyes nowadays account for ~50% of global dye consumption for cellulosic fibres compared to just 10% by direct dyes[131] (Figure 4).

Although in more recent times, the remarkable levels of innovation in both the chemistry and application of dyes that occurred from the late nineteenth century upto the mid twentieth century has slowed, noticeably, especially in the case of the development of novel commercial dye products, it nevertheless fuelled the current seemingly unrelenting fascination with increased levels of performance demanded by retailers, and apparently consumers, of dyed materials.

Using the summary of global cellulosic fibre production as a proportion of total world fibre production in 2017 presented in Figure 3, an estimate can be made of the amount of dye that was likely consumed in 2017 to dye cotton and various types of man-made cellulosic fibre, based on the assumptions that because a sizeable proportion of undyed cellulosic fibre is employed in, for example, apparel and home furnishings, such as shirting, bedding, etc., then of the ~31×10^6 T of natural and man-made cellulosic fibre produced in 2017,[1] around 75%, which equates to ~23.3×10^6 T, will likely have

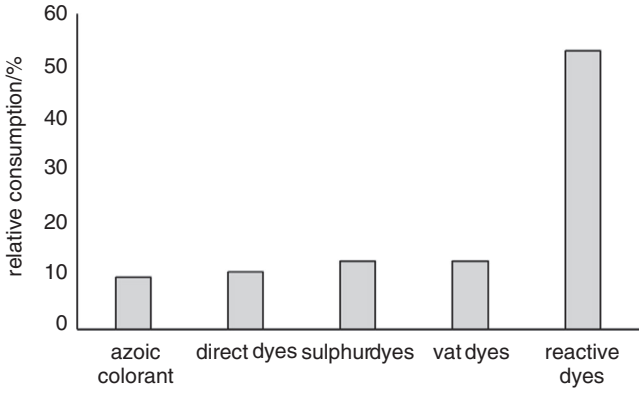


FIGURE 4 Estimated consumption of different dye classes for cellulosic fibres; drawn using data from[131]

been dyed and an average 2% omf (on mass of fibre) depth of shade[19] would have been applied to these cellulosic fibres. Accordingly, based on the dye class consumption data presented in Figure 4, the amounts of each of the five classes of dye that may have been consumed to dye cotton, CLY, CV, etc. in 2017 are shown in Table 3; the dominance of reactive dyes is clearly evident.

2.3.2 | Dyeing characteristics

The main reason that such a wide range of dye classes continue to be employed for cellulosic fibres is that the different dye classes offer dyers the opportunity to produce dyeings that meet a wide range of end-use requirements (eg fastness, brightness, cost, etc.). However, because vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes differ in terms of their structure (eg chemical class, molecular size, planarity, etc.) and both chemical and physical properties (eg type/number of hydrophilic group, thermal sensitivity, reactivity, etc.), the five classes of dye display characteristically different adsorption behaviour on a given type of cellulosic fibre, which necessitates the use of different application conditions (pH, temperature, alkalinity, etc.).

Moreover, at the end of an exhaust dyeing process, the dyes are present within the substrate in one of three different physical states, namely as:

- *insoluble colourant* (vat dyes and azoic colourants);
- *low solubility colourant* (direct dyes and sulphur dyes);
- *covalently bound colourant* (reactive dyes).

As the level of fastness displayed by a given dyeing to wet treatments, such as water, perspiration, washing, etc., to a first approximation, reflects the ability of the dye to desorb from the dyed substrate into the surrounding aqueous environment, it follows that the fastness of the five classes of dye on cellulosic fibres to wet treatments generally decreases in the order[19]:

vat dyes = azoic colourants =/> reactive dyes >> sulphur dyes > direct dyes

2.4 | Dyeing conditions used

As mentioned, because the five dye classes differ structurally and possess a diverse range of chemical and physical properties, markedly different application conditions are employed for their exhaust application to cellulosic fibres, as illustrated by the data presented in Table 4.

The multiplicity of dyeing conditions listed in Table 4 for the various types of dye/dye precursor, reflects the significant, structure-related and property-related differences exhibited by the five classes of dye (eg solubility, functional group content, etc.), which, in turn, are responsible for the different types of dye displaying markedly different adsorption behaviour on cotton that necessitates the use of different application conditions (pH, temperature, etc.).

Whilst the particular dyebath conditions utilised will vary according to three main processing variables, namely the type of fibre (eg cotton, CV, etc.), the gross physical structure of the textile material (eg yarn, woven fabric, knitted/woven towelling, etc.) and type of dyeing machine utilised (eg jet, beam, etc.), variations in both the temperature (or rather, temperature range) and pH (or commonly, pH range) employed for dyeing also arise because each of the different classes of dye have specific application requirements, such as, for example, the need to utilise a particular pH range, employ a specific type of reducing agent, use a certain dyeing temperature, etc.

2.4.1 | Number of dyeing stages

It is apparent from Table 4 that for each of the five dye classes under consideration, dyeing is a *multi-stage process*. For example, azoic colourants are water-insoluble *azo compositions* that are generated *in situ* within the cellulosic fibre by means of a two-stage application process. In the first stage, referred to as *naphtholation*, a water-insoluble *azoic coupling component*, Ar-OH, is converted into the corresponding, water-soluble, ionised *naphtholate* variant, $Ar\text{-}O^-$, by dissolution in NaOH, and the naphtholate derivative is applied to the fibre. In the second stage of the application process, referred to as

Dye class	Usage on cellulosic fibres/ %	Amount of cotton dyed/ $\times 10^6$ T	Amount of dye used/ $\times 10^3$ T
Azoic colourant	10	2.3	46.5
Vat	13	3.0	60.5
Sulphur	13	3.0	60.5
Direct	11	2.6	51.1
Reactive	53	12.3	246.6
Total	**100**	**23.3**	**465.2**

TABLE 3 Estimated amounts of each of the five classes of dye used for dyeing cellulosic fibres in 2017 based on dye consumption data from[131] and assuming[19] 75% of the 2017 global cellulosic fibre production of ~31×10^6 T [44] was dyed to an average 2% omf depth of shade

TABLE 4 Typical exhaust dyeing conditions employed for cellulosic fibres together with indicative overall fastness level of dyeings

Dye class	Number of dyeing stages	Dyebath pH	Dyeing temperature/ °C	Main dyeing auxiliaries used[a]	All-round level of fastness	Dye solubility in the dyebath	After treatment usually required
Azoic colourant	2	12-13/4-7[b]	15-30/5-15	NaOH; NaCl	Excellent	Very high	No
Vat	3	12-13	20-60	NaOH; NaCl; reducing agent; oxidising agent	Excellent	Very high	No
Sulphur[c]	2-3[d]	10-11	60-90	NaCl/Na_2SO_4; reducing agent; oxidising agent	Good/very good[e]	High/moderate	Yes
Direct	1-2[d]	6-7	80-98	NaCl/Na_2SO_4	Moderate/ good[e]	Moderate	Yes
Reactive	2	10-12	30-95	NaCl/Na_2SO_4; NaOH/ Na_2CO_3	Very good/excellent	High/very high	No

[a]Dye makers usually recommend specific types of *auxiliary chemical* (aka *auxiliary*) for their particular dye ranges.
[b]*Naphtholation stage* and subsequent *development stage* carried out under different pH conditions, namely alkaline and acidic/weakly acidic, respectively.
[c]The application conditions employed vary according to the particular sulphur dye variant utilised, namely *sulphur dye*, *leuco sulphur dye* or *solubilised sulphur dye*.
[d]Includes a specific *aftertreatment*.
[e]As the result of a specific aftertreatment.

development, the water-insoluble azoic coupling component, Ar-OH, is *regenerated* within the fibre by neutralisation, and the desired, water-insoluble azoic composition, HO-Ar-N=N-Ar', is then formed in situ within the substrate as the result of the *diazo coupling reaction* between the azoic coupling component and an *azoic diazo component*, Ar'-$N^+\equiv$N (ie *diazonium salt*).[19] As the ensuing azoic composition, HO-Ar-N=N-Ar', is insoluble, so azoic colourants display typically excellent levels of wet fastness on cotton and other types of cellulosic fibre (Table 4).

Both vat dyes and sulphur dyes are also applied to cotton using two-stage processes (Table 4) that involve the initial application of the respective soluble *dye anion derivative* and the subsequent conversion, in situ, to either the insoluble (vat dyes) or sparingly soluble (sulphur dyes) variant. Briefly, although vat dyes are insoluble and exhibit little, if any, substantivity towards cotton, as they contain two or more conjugated *keto groups*, -C=O, the dyes can be converted, by means of reduction under alkaline conditions, to the substantive, anionic, water-soluble *enolate*, -C-O^-, derivative, often referred to as the *leuco derivative*, in which form the dyes are applied to the cellulosic substrate. In the second stage of the dyeing process, oxidation converts the soluble enolate form of the dye, -C-O^-, to the parent, insoluble, keto form of the dye, -C=O, in situ within the fibre.

A similar two-stage process is employed for sulphur dyes in so far as the structurally complex, low solubility, poorly substantive, macromolecular dye molecules, which comprise multiple *thiol groups*, -SNa, are initially reduced under alkaline conditions to the substantive, soluble, anionic *thiolate* derivative, -S^-, in which form the dyes are applied to the cellulosic fibre. During the second stage of dyeing, the soluble thiolate derivatives, -S^-, are oxidised, thereby generating the sparingly soluble disulfide (-S-S-) and/or oligosulfide ([-S-S-]$_n$) form of the sulphur dye, in situ. In the case of solubilised sulphur dyes, the thiosulphuric acid derivative, -SSO_3^-, of the parent sulphur dye is converted to the thiolate form of the dye, -S^-, during dyeing: subsequent oxidation during the second stage of dyeing generates the sparingly soluble disulfide/oligosulfide form of the parent sulphur dye, in situ.[19,61]

As the regenerated enol form of vat dyes that is formed within the cellulosic substrate is insoluble, so vat dyes characteristically exhibit excellent levels of fastness on cotton. In contrast, because the disulfide/oligosulfide derivatives of sulphur dyes are *sparingly soluble*, sulphur dyes tend to display only characteristically moderate levels of fastness on cotton and other types of cellulosic fibre (Table 4).

Furthermore, because of their amphiphilic, planar structure, azoic colourant, vat dye and sulphur dye molecules each exhibit an innate disposition to *self-associate*. For example, it is well-known that vat dyes display an inherent tendency to self-associate in situ within dyed cellulosic fibres,[132,133]

with the result that *dye particles* are formed which comprise aggregates of vat dye molecules. As the vat dye particles are insoluble, so dye aggregation can be expected to further contribute to the characteristic excellent wet fastness exhibited by vat dyes on cellulosic fibres. In a similar vein, the sparingly soluble, large molecular size disulfide/oligosulfide derivatives of sulphur dyes can also be expected to self-associate, as has been observed in the case of their application to polyamide fibres.[134]

In marked contrast to their azoic colourant, vat dye and sulphur dye counterparts, direct dyes are both soluble and substantive towards cellulosic fibres. Consequently, the dyes do not require initial conversion to a soluble, substantive form, but, instead, as recounted, can be applied to cotton using a single-stage process (Table 4). Although direct dyes carry multiple sulphonate/sulphonic acid groups, $-SO_3Na/-SO_3H$, and therefore, display high solubility, they also exhibit a marked tendency to self-associate.[19] The latter characteristic structural attribute of direct dyes is of major significance in terms of the particular physical orientation which the dyes adopt within the dyed substrate insofar as, once the dyes have been applied to the cellulosic fibre and the desired depth of shade secured, the intrinsic predisposition of the adsorbed dye molecules to self-associate in situ within the dyed fibre is encouraged during the final cooling phase of the single-stage dyeing process, owing to the endothermic nature of dye aggregation processes. However, although the ensuing large molecular size, direct dye aggregates within the fibre display reduced solubility compared to their non-aggregated single dye molecule progenitors, the aggregated dye molecules nevertheless exhibit only moderate fastness to wet treatments (Table 4) because they are merely physically retained within the substrate and, as a consequence, are able to diffuse out of the dyed material during, for example, domestic laundering.

Reactive dyes bear a strong structural resemblance to direct dyes, insofar as they not only derive their inherently high solubility from the presence of sulphonate/sulphonic acid groups and do not require conversion to a soluble, substantive form, but the dyes also exhibit a distinct tendency to self-associate. However, in contrast to their direct dye counterparts, reactive dyes comprise a *reactive system* which necessitates the use of a two-stage application process (Table 4). During the first stage of dyeing, the dyes are applied under alkaline conditions which generate nucleophilic, ionised hydroxyl groups, $Cell\text{-}O^-$, within the cellulosic substrate with which *electrophilic groups*, $-X^{\delta+}$, in the reactive system within the dye molecule are able to form a covalent bond, Cell-O-dye. During the second stage of the dyeing process, the dyed material is subjected to a robust *wash-off process* that removes non-covalently bound dye, so that, ideally, the ensuing dyed fibre contains only covalently attached dye molecules. Because the dyes are covalently attached to the component cellulose macromolecule, reactive dyes exhibit characteristically very good/excellent levels of wet fastness on cellulosic fibres (Table 4).

In the cases of both direct dyes and sulphur dyes, an additional *aftertreatment* stage is typically required in order to secure optimum levels of fastness towards wet treatments encountered during usage (Table 4), such as laundering, perspiration, etc.; such aftertreatments usually involve the application of specific proprietary compounds which impart enhanced levels of wet fastness to the dyed cellulosic material.[19,135-143]

The above brief discussion reveals that dye self-association is a common feature of each of the five classes of dye used on cellulosic fibres. Indeed, as discussed in the second part of the article, as most classes/types of dye exhibit an instinctive disposition to self-associate[19] so dye aggregation is encountered in virtually all dye/fibre systems. Importantly, as is also explained in the next part of the article, dye self-association plays a critically significant role in the promotional effect imparted by added inorganic electrolyte to the uptake of azoic colourants, vat dyes, sulphur dyes, direct dyes and reactive dyes on cellulosic fibres.

2.4.2 | Temperature and pH

Table 4 shows that in the case of azoic colourants, low temperatures (or rather a low temperature range), can be utilised for each of the two application stages involved (ie *naphtholation* and *development*). This can be attributed to the high aqueous solubility of both the naphtholate, $Ar\text{-}O^-$, and diazonium salt, $Ar'\text{-}N^+{\equiv}N$, coupled with the relatively small molecular size of the two types of azoic component involved. Of course, the in situ diazotisation reaction that leads to the formation of the desired azoic composition can only be undertaken at very low temperature (~5-15°C).

Table 4 also reveals that low temperatures can be used to apply enolate vat dye derivatives, $-C\text{-}O^-$, to cellulosic substrates, which once again can be attributed to the high solubility of the ionised dye variant, as proposed in the case of azoic colourants. However, in contrast to the small molecular size of both azoic coupling components and azoic diazo components, vat dyes are typically large, planar molecules prone to self-association. Therefore, the ability to apply vat dyes at low temperatures cannot be ascribed primarily to their small molecular size. Instead, it seems reasonable to suggest that as the application of vat dyes is carried out under alkaline conditions, which are typically achieved using NaOH, the ability to apply the large molecular size enolate anions, $-C\text{-}O^-$, at low temperatures may be attributable to the effect which alkali and, in particular NaOH, exerts upon the cellulosic substrate. In the latter context, as azoic coupling components are also applied under strongly alkaline conditions, commonly realised using NaOH, perhaps the ability to apply naphtholate

derivatives, Ar-O$^-$, to cellulosic fibres at low temperatures (Table 4) may in some part also be a corollary of the effect of alkali on the cellulosic substrate.

In this context, as previously discussed in Section 2.2.4, cellulosic fibres swell readily when immersed in water because the adsorbed water molecules weaken both intermolecular and intramolecular H-bonds between -OH groups located within the amorphous regions of the substrate, resulting in intercrystalline swelling; however, the water molecules are unable to penetrate the crystalline domains within the fibre. When immersed in concentrated aqueous NaOH solution, cotton and other types of cellulosic fibre swell to a much greater extent than in water alone because the water molecules are able to penetrate both the amorphous domains and the crystalline regions of the substrate, so that intercrystalline swelling is accompanied by intracrystalline swelling, in which H-bonds between hydroxyl groups in the crystallites are weakened. This characteristic alkali-induced swelling of cellulosic fibres that occurs when immersed in concentrated solutions of NaOH is the basis of the mercerisation process[19] that is widely used to impart desired chemical and physical modifications to the fibres, including, for example, enhanced adsorption of each of the five classes of dye under consideration. However, significant alkali-induced cellulosic fibre swelling occurs only at very high NaOH concentrations, of the order 2-3 mol l^{-1} (80-120 g l^{-1}) in the case of the mercerisation process for cotton,[144,145] which is much greater than that utilised in the application of either vat dyes or azoic coupling components, which ranges, typically, between ~1 and 10 g/L. Consequently, it seems unlikely that the use of alkali, in the guise of NaOH, is a major reason why vat dyes and azoic coupling components can be applied to cellulosic substrates at low temperatures.

A more plausible explanation can be proffered by assuming that it is the aqueous alkaline dyebath application conditions, or more specifically, the resulting high aqueous solubility of both the enolate derivative of vat dyes and the naphtholate form of azoic coupling components under the particular alkaline dyebath conditions employed, that enable low temperatures to be utilised for their application. In this context, vat dyes are usually classified by dye makers according to the level of substantivity displayed by the leuco form of the dye towards the particular type of cellulosic fibre, which determines both the temperature at which the dyes are applied and the amount of alkali required for dyeing. For example, enolate derivatives of vat dyes which display inherently low dye-fibre substantivity are applied at low temperatures (20-30°C) in the presence of small amounts of alkali, whereas temperatures in the region of 60°C are utilised for higher substantivity leuco derivatives that require the use of greater amounts of alkali. Because the lower substantivity enolate variants possess higher solubility in the aqueous alkaline dyebath than their lower solubility, higher substantivity counterparts, can, therefore, be applied at lower temperatures.

Thus, it seems reasonable to propose that it is the high aqueous solubility of the anionic enolate vat dye derivative (-C-O$^-$) and the anionic azoic coupling component (Ar-O$^-$) in the aqueous, alkaline dyebaths that enable low temperatures to be utilised for their application.

The fact that high temperatures are characteristically used to apply sulphur dyes to cellulosic fibres (Table 4), even though strongly alkaline conditions are typically employed, can be attributed to the large molecular size of the thiolate derivatives. As mentioned, sulphur dyes are complex macromolecules of mostly unresolved structure; when reduced under alkaline conditions, it is probable that a variety of similarly complex, heterogeneous, oligomeric and/or macromolecular, thiolate derivatives, -S$^-$, are generated which can be expected to display characteristically low rates of diffusion within the amorphous regions of the cellulose polymer. As such, it can be anticipated that high dyeing temperatures will be required to promote the diffusional behaviour of the large molecular size, soluble thiolate molecules.

The fact that reactive dyes characteristically display high solubility under the typically strongly alkaline conditions utilised for dyeing (Table 4), can also be considered to explain why low temperatures, in the region of ~30°C, can be employed in immersion dyeing processes. That higher dyeing temperatures are also utilised for some types of reactive dye (Table 4) reflect the fact that a wide range of commercial ranges of reactive dye are available which vary markedly in terms of, for example, their substantivity, diffusional behaviour, sensitivity to added electrolyte, *reactivity* of the particular electrophilic reactive system(s) carried by the dye molecules, so the immersion dyeing behaviour of the dyes varies markedly in terms of the temperature, pH, type of alkali, etc. required to expedite the desired extents of exhaustion, levelness and reaction with the substrate.

The facts that high dyeing temperatures, of the order of 80 to 98°C (in some cases upto 120°C), in conjunction with essentially neutral dyebath conditions, are used to apply direct dyes to cotton (Table 4), can be attributed to the inherent predisposition of the large molecular size, planar dye molecules to self-associate in aqueous solution, coupled with the fact that owing to the endothermic nature of the dye aggregation process, the extent of dye self-association decreases with increasing temperature. Thus, at low dyeing temperatures, the direct dye dyebath will comprise a high proportion of direct dye aggregates that display low solubility and correspondingly low diffusional behaviour; in such a case, dye–fibre substantivity will be low. As dyeing temperature increases and dye aggregation decreases, so the proportion of low solubility dye aggregates reduces and the number of high solubility direct dye anions, which display high diffusivity, will increase accordingly, with the result that dye–fibre

substantivity increases. Thus, it seems reasonable to suggest that because of the intrinsic tendency of direct dyes to self-associate and the corresponding low aqueous solubility of the ensuing direct dye aggregates in the aqueous dyebath, high dyeing temperatures are typically used to apply direct dyes to cotton.

The above brief discussion implies that the particular temperature employed to dye cellulosic fibres using the five dye classes under consideration is primarily determined by the solubility of the given type of dye in the aqueous dyebath. In essence, the higher the solubility of the dye in the dyebath, the lower the temperature that can be used for dyeing: such a solubility/temperature relationship is demonstrated by the correlation of the data presented in columns four and seven in Table 4. Indeed, as mentioned, from the viewpoint of the role of inorganic electrolyte in cellulosic fibre dyeing, the solubility of the dye/dye precursor anion in the dyebath is of crucial importance, as discussed in the second part of the article.

2.4.3 | Physical form of the dye in the dyebath and fibre

The discussion in Section 2.4.1 revealed that the five types of dye/dye precursor vary in terms of the physical state in which they are present within both the aqueous dyebath and the dyed substrate, this situation being summarised in Table 5.

Even though members of each of the five dye classes are adsorbed by the substrate in the form of dissolved dye anions (ie phenolate and diazonium salt, enolate, thiolate or sulphonate), the characteristic level of substantivity displayed by the five different classes of dyes towards the cellulosic substrate varies, as reflected by the different application conditions (pH and temperature) that are typically employed in dyeing (Table 4).

TABLE 5 Typical characteristics of dye classes used for dyeing cellulosic fibres

Dye class	State within aqueous dyebath	State within dyed substrate
Vat	Enolate: -C-O^-	Insoluble: dye-C-OH
Sulphur	Thiolate: -S^-	Low solubility: dye-S-S_n
Azoic colourant	Phenolate: Ar-O^-/ diazonium salt, Ar'-$N^+\equiv$N	Insoluble: HO-Ar-N=N-Ar'
Direct	Sulphonate: -SO_3^-	Low solubility: dye-SO_3Na
Reactive	Sulphonate: -SO_3^-	Covalently attached: Cell-O-dye-SO_3Na

As mentioned, each of the initial stages of the application of azoic colourants, vat dyes, sulphur dyes and reactive dyes, as well as the single-stage application of direct dyes, consists of the transfer of the dissolved, high solubility, dye anion (phenolate, enolate, thiolate or sulphonate variant) through the aqueous dyebath phase to water-filled, swollen, amorphous domains located within the semi-crystalline cellulose polymer, wherein the dye/dye precursor anions diffuse, interact with appropriate -OH groups located within the constituent cellulose polymer chains and, eventually, become adsorbed. The conditions required to expedite this aqueous-based transfer process clearly vary for the five dye classes (Table 4), in accord with factors related to, for example, the molecular size of the dye anions, their solubility, the degree of dissociation of the component functional groups, etc.

In contrast, as recounted earlier, at the end of the respective second stage of dyeing, the dyes are present in the fibre phase in the form of either:

- insoluble colourants: via the generation of the insoluble azo compound (OH-Ar-N=N-Ar': azoic colourants) or regeneration of the insoluble enol variant (-C-OH: vat dyes) in situ within the substrate, so the ensuing dyeings display characteristically very high wet fastness;
- low solubility colourants: via the in situ conversion of the high solubility thiolate derivative of sulphur dyes (-S^-) to the lower solubility, disulfide/oligosulfide variant and the self-association of direct dyes in situ within the dyed substrate;
- covalently bound colourants: via the in situ formation of one or more covalent bonds between a reactive dye and the substrate (Cell-O-dye).

Because, as mentioned, vat dyes, azoic colourants, sulphur dyes, direct dyes and reactive dyes exhibit a distinct tendency to self-associate and, crucially, as it is well-known that such dye aggregation is encouraged in the presence of inorganic electrolyte, it follows that a possible role for added NaCl or Na_2SO_4 in cellulosic fibre dyeing is to promote the extent of dye self-association within the dyebath phase which will reduce the intrinsically very high solubility of the dye/dye precursor anion in the dyebath and thereby result in increased dye–fibre substantivity. However, whilst this mechanism may seem reasonably straightforward, the precise manner by which reduced dye solubility/enhanced dye aggregation in the dyebath lead to increased dye uptake in the fibre phase is not at all uncomplicated, as discussed in the next part of the paper.

2.4.4 | Amount of water

The dyeing of cellulosic fibres routinely consumes substantial amounts of water,[19] as is typically observed for many

other types of wet processes that the fibres undergo during their transformation from raw fibre/raw material to finished yarn, fabric, etc. [19,146-148]; this is illustrated by the data presented in Table 6 for the most popular of all types of cellulosic fibre, cotton.

In Table 6, column three provides an estimate of the amount of water that can be expected to have been consumed in each of the various cotton wet processes considered, based on the data of Correia *et al*[149] in column two and assuming global cotton production in 2017 was 25.5×10^6 T,[44] of which 75% (~19.1×10^6 T) may have been dyed[19] using the earlier five classes of dye under consideration. Clearly, the scale of water usage is astonishingly high, with total consumption being of the order of between ~7 and 28 billion Tonnes.

In the context of exhaust dyeing, the amount of water that is used in a particular dyeing process is described by the parameter *liquor ratio* (or *goods/liquor ratio*), which simply expresses the ratio of the amount of substrate used to the amount of water used. For example, in an immersion dyeing process that utilises a liquor ratio of 1:5 then for every 1 kg of fibre dyed, 5 L or 5 kg of dye solution will be used (assuming the approximate equivalence of 1 L of water = 1 kg of water).

A range of factors influence the choice of liquor ratio selected for dyeing, including those related to the substrate (eg type of fibre, material construction, fabric density, etc.), dye (eg class/type, depth of shade, etc.), dyeing machine, cost/availability of water, etc.[19] For immersion dyeing processes in general, lower liquor ratios promote both the rate of dyeing and the extent of dye uptake (Figure 5) whilst higher liquor ratios promote dye levelling, expedite dye solubility, etc. during dyeing.

A wide range of liquor ratios are utilised in commercial exhaust dyeing processes: for example, the liquor ratio employed in contemporary jet dyeing machines for the dyeing of knitted cotton fabric is 1:8-1:10 with *Best Available Technology* (BAT) machines offering the ability to use a 1:3-1:4 liquor ratio. Indeed, the water usage data presented in Table 6 show that the liquor ratios employed for the various types of cotton wet process varied widely, from 1:3 to a cumulative 1:308. The reason why such copious amounts of water are consumed in cotton wet processing, including dyeing, for which the very high liquor ratio of 1:300 was reported (Table 6), reflects *cumulative water usage* insofar as, a particular processing stage, such as bleaching or dyeing, for example, typically involves the use of ancillary wet processes such as rinsing/washing, etc., that are necessary components of the particular bleaching or dyeing stage. Whilst this goes some way to explain why such vast amounts of water are consumed in cotton wet processing, it does not in any way justify or excuse such enormous, accumulated water usage.

As liquor ratio determines the volume of an aqueous exhaust dyebath, it follows that the parameter also controls both the concentration and amount of the various components of the dyebath, notably that of dyes and dyeing auxiliary chemicals (eg alkali, buffer, etc.); indeed, as discussed in the following two sections, dyebath volume and the amount/concentration of dyebath components are intrinsically linked via liquor ratio.

TABLE 6 Average water usage for cotton wet processes

Process	Water usage/ l kg^{-1} [149]	Water usage consumed in 2017/ T
Desizing	3-9	[a] 7.7×10^7-2.3×10^8
Scouring	26-43	[a] 6.6×10^8-11.1×10^9
Bleaching	3-124	[a] 7.7×10^7-3.2×10^9
Mercerising	232-308	[a] 5.9×10^9-7.9×10^9
Dyeing	8-300	[b] 1.6×10^8-5.8×10^9
Total		**6.9×10^9-28.1×10^9**

[a]Assumes ~25.5×10^6 T of cotton produced in 2017[44] was processed.

[b]Assumes 75% of cotton produced in 2017 (ie ~19.1×10^6 T) was dyed.

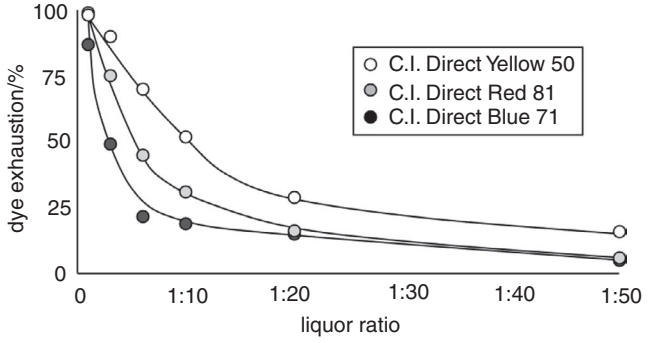


FIGURE 5 Effect of liquor ratio on uptake of commercial direct dyes on cotton in the absence of added inorganic electrolyte; drawn using data from[150]

2.4.5 | Amount of dye

The amount of dye employed in a given immersion dyeing process is normally calculated on the basis of the mass of fibre used, expressed by the term omf; depths of shade are commonly referred to as pale < 2% omf, medium 2% omf and deep > 2%.[19]

Because, as mentioned, the liquor ratio selected for dyeing determines the volume of the aqueous dyebath, in that the volume of dyebath liquor decreases with decreasing liquor ratio (Table 7), as the amount of dye employed for dyeing is based on the mass of the fibre used (ie omf) rather than the volume of the dyebath, so the concentration of the dye in the dyebath varies, depending on the amount of water employed for dyeing, as defined by liquor ratio.

This means that the manner by which the dye functions, as expressed in terms of its solubility, migration ability, etc.,

TABLE 7 Simple representation of the effect of liquor ratio on dyebath volume and dyebath dye concentration for a 2% omf and 5% omf dyeing of 1 kg of fibre

Liquor ratio	Dyebath volume/ l	Dye concentration/ g l^{-1}	
		2% omf dyeing	5% omf dyeing
1:100	100	0.2	0.5
1:50	50	0.4	1
1:10	10	2	5
1:5	5	4	10
1:1	1	20	50

also varies according to the liquor ratio selected for use. This accounts for the facts that, generally, higher liquor ratios (eg 1:100, 1:50, etc.) furnish slow rates of dye uptake which encourage dye migration and favour level dyeing, whereas lower liquor ratios (eg 1:5, 1:3, etc.) provide high dyeing rates which promote dye uptake but offer generally low levels of dye migration.

2.4.6 | Amount of dyeing auxiliaries

Table 4 shows that specific types of auxiliary chemical are utilised for the immersion application of each of the five dye classes. Briefly, auxiliaries are added to aqueous dyebaths in order to provide a highly specific form of assistance to the exhaust dyeing process, insofar as the particular auxiliary chemical is designed to augment/promote/negate/diminish a particular attribute of the dye–fibre system, such as fibre wetting, dye migration, fibre fibrillation, etc.[18] As such, many types of dyeing auxiliary are utilised in commercial immersion dyeing processes (eg dispersants, deaeration agents, solubilising agents, etc.) which comprise a heterogeneous group of chemical types (eg surfactants, reductants, buffers, etc.). Accounts are available of the various types of auxiliary that are utilised in immersion dyeing processes, including those for cellulosic fibres, the nature of the assistance they impart, as well as both environmental and financial aspects related to their use.[18,143,151-156]

Table 4 also reveals that in the case of the exhaust dyeing of cellulosic fibres, whilst specific auxiliaries such as reducing agents, oxidants and alkali are required for the application of some dye classes, notably vat dyes and sulphur dyes, one particular type of auxiliary chemical is common to each of the dye classes, namely *inorganic electrolyte*, in the form of either NaCl or Na_2SO_4. Indeed, as mentioned, added inorganic electrolyte exerts a remarkable promotional effect on the uptake of azoic coupling components, vat dyes, sulphur dyes, reactive dyes and direct dyes. As such, inorganic electrolyte is widely believed to be the most crucially important, indispensable, auxiliary chemical employed in the application of each of the five dye classes, despite the fact that the manner by which added inorganic electrolyte (which is commonly, and wrongly, referred to as *salt*) promotes dye/dye precursor adsorption, is widely mis-understood and the precise nature of its outstanding promotional effect on dye uptake has only recently been finally resolved in the case of direct dyes[131,150,157,158] and reactive dyes.[125,159-161]

As the role of added inorganic electrolyte in cellulosic fibre dyeing is the primary focus of this article, this discussion of dyeing auxiliaries employed in dyeing is confined to that of NaCl or Na_2SO_4.

2.5 | Inorganic electrolyte

As recounted, each of the five types of dye/dye precursor are applied to cellulosic fibres as anions, namely phenolate ions, $Ar\text{-}O^-$, in the case of azoic coupling components, sulphonate anions, $\text{-}SO_3^-$, for both direct and reactive dyes and thiolate, $\text{-}S^-$, and enolate, $\text{-}C\text{-}O^-$, anions, respectively, in the cases of sulphur dyes and vat dyes. However, each of these various anionic species typically display characteristically low substantivity towards cotton and other types of cellulosic fibre: consequently, for each type of dye/dye precursor, inorganic electrolyte in the form of either NaCl or Na_2SO_4, is added to the aqueous dyebath in order to promote dye–fibre substantivity and, thereby, ensure that adequate levels of dye uptake are secured.

Inorganic electrolyte has been employed in dyeing cellulosic fibres for millennia: in the latter context, owing to the overwhelming prevalence of the word *salt* in connection with the dyeing of cellulosic fibres, it was decided that the title of this article should include the term *salt* as well as the correct term for this particular type of dyeing auxiliary (ie NaCl or Na_2SO_4), namely *inorganic electrolyte*.

The promotional effect imparted by added inorganic electrolyte on dye uptake, which is illustrated by the findings presented in Figure 6, is viewed as a fundamental, mandatory aspect of the dyeing of cellulosic fibres using azoic coupling components, vat dyes, sulphur dyes, reactive dyes and direct dyes. Indeed, the unquestioned reliance of NaCl or Na_2SO_4 in cellulosic fibre dyeing and the presumption that the use of this seemingly simple, inexpensive, readily available chemical is not only indispensable but also entirely acceptable from economic, technical and, more importantly, environmental perspectives, is illustrated by the fact that the previously recounted commercial introduction of direct dyes in 1884 was unconditionally based on the fundamental premise that adequate levels of dye uptake could be achieved only via the promotional effect of added inorganic electrolyte: exactly the same automatic presumptions regarding the use of added NaCl or Na_2SO_4 in cellulosic fibre dyeing were made

in the case of reactive dyes when they were commercially introduced in 1956.

2.5.1 | The scale of inorganic electrolyte usage in cotton dyeing

Three types of inorganic electrolyte can be used in cellulosic fibre dyeing:

1. Sodium chloride (NaCl).
2. Anhydrous (aka calcined) sodium sulphate (Na_2SO_4).
3. Sodium sulphate decahydrate (Glauber's salt, $Na_2SO_4 \times 10H_2O$).

The selection of which inorganic electrolyte should be utilised for dyeing (1 kg of NaCl ≡ 1.22 kg Na_2SO_4 ≡ 2.78 kg $Na_2SO_4 \times 10H_2O$[131]) is often based on, for example, cost, availability and even historical preference, though dye makers often recommend a particular type of inorganic electrolyte for use with members of a given commercial dye range (Table 8).

Because the amount of NaCl or Na_2SO_4 required for an immersion dyeing processes typically varies for different commercial ranges of dye, type of fibre, dye machine, etc., so dye makers commonly prescribe not only the type of inorganic electrolyte, but also the amount of NaCl or Na_2SO_4 required for their particular commercial dye range.

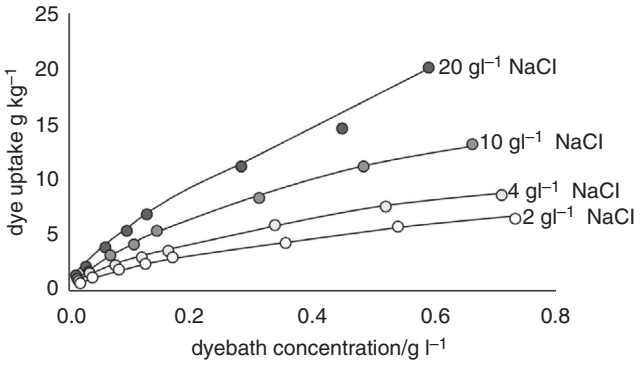


FIGURE 6 Effect of different concentrations of added NaCl on equilibrium uptake of purified CI Direct Yellow 12 on CV sheet at 97.5°C; drawn using data from[162]

In the latter context, the amount of added inorganic electrolyte required for exhaust dyeing depends on, for example, the relative substantivity of the dye used, amount of dye applied (eg, nature of the particular dye range (e.g. Class A, B or C direct dye, low/medium/high reactivity reactive dye, class of sulphur dye, etc.), and type of cellulosic substrate (Table 8), as well as the type of dyeing machine and liquor ratio (Table 9).

As the quantity of NaCl or Na_2SO_4 employed in a particular dyeing process is usually calculated on the basis of *dyebath concentration*, commonly expressed in terms of grams per litre (Tables 8 and 9), it follows that both the *nature* and *extent* of the promotional effect imparted by the added electrolyte is markedly *concentration-dependent*. As such, the liquor ratio selected for dyeing determines the amount of inorganic electrolyte required for dyeing insofar as, the aqueous dyebath must contain the recommended, crucially important concentration of NaCl or Na_2SO_4 required to impart the desired level of dye uptake promotion, *irrespective* of the amount of water present in the aqueous dyebath. It follows that as the volume of an aqueous dyebath increases with increasing liquor ratio so the quantity of the chosen electrolyte required for dyeing must also increase in order to achieve the desired concentration of NaCl or Na_2SO_4 in the dyebath.

This situation is illustrated by Table 10 which shows how the amount of, for example, NaCl required for dyeing 1000 kg of cotton, varies as a function of the liquor ratio employed for dyeing. Table 10 reveals the significant impact which liquor ratio can impart to exhaust dyeing processes for cellulosic fibres, from the viewpoints of both the cost and environmental aspects of dyeing. High liquor ratios present major economic challenges, not simply because of the direct costs of the greater amounts of both water and inorganic electrolyte used, but also due to the higher indirect costs associated with remediating the large volumes of wastewater that possess significant levels of salinity.[18] Moreover, inorganic electrolyte exerts a corrosive effect on the stainless steel that is utilised in modern dyeing machines.

As previously discussed (Table 4), the five classes of dye under consideration vary, widely, in terms of the conditions that are employed for their exhaust application (eg temperature, pH, etc.). Unsurprisingly, the five types of dye also

TABLE 8 Amount of added inorganic electrolyte and alkali required for exhaust dyeing of cellulosic fibres using [a] *Duractive V* (*Town End Colours*) reactive dyes[163] and [b] *Tulactiv XLE* (Atul) reactive dyes[164]

	NaCl/ gl^{-1}		NaCl/ gl^{-1}		
% omf dye	NaCl/ gl^{-1}	Na_2CO_3/ gl^{-1}	Cotton	Mercerised cotton and viscose	Na_2CO_3/ gl^{-1}
≤0.5	20[a]	1.5[a]	45[b]	30[b]	10[b]
0.5-2.0	30[a]	3[a]	60[b]	40[b]	15[b]
2.0-4.0	40[a]	5[a]	70[b]	55[b]	20[b]
>4.0	50[a]	7[a]	90[b]	65[b]	20[b]

TABLE 9 Amount of added inorganic electrolyte and alkali required for exhaust dyeing of cellulosic fibres using *Duractive H* (Town End Colours) reactive dyes at 40°C[165]

	Circulating machine	Winch machine
Liquor ratio	1:8-1:12	1:15-1:30
NaCl/ gl^{-1}	50-80	50-80
NaOH 72°Tw/ cm^3 l^{-1}	2-3	40
Trisodium phosphate g l^{-1}	15-20	10-15

TABLE 10 Idealised representation of the effect of liquor ratio on the amount of added sodium chloride (NaCl) required to dye 1000 kg of cotton to a 2% omf depth of shade, assuming usage of 50 g l^{-1} and 80 g l^{-1} NaCl

		Amount of NaCl required/ kg	
Liquor ratio	Amount of water used/ l	50 g l^{-1} NaCl	80 g l^{-1} NaCl
1:3	3000	150	240
1:5	5000	250	400
1:10	10 000	500	800
1:50	50 000	2500	4000

TABLE 11 Typical amounts of sodium chloride (NaCl) required for immersion dyeing of cotton according to dye class

Dye class	Typical amount of NaCl used in dyeing cotton/ g l^{-1}
Vat	5-40
Sulphur	5-20
Azoic colourant	10-40
Direct	5-15
Reactive	30-100

vary in terms of the amount of added inorganic electrolyte required for their immersion application to cellulosic fibres (Table 11).

Of the five dye classes, the largest amounts of added inorganic electrolyte are typically consumed in the exhaust application of reactive dyes (Table 11). As this class of dye is nowadays the most popular for dyeing cotton (and other types of cellulosic fibre), accounting for some 53% of global usage [131] (Figure 3), it follows that such widespread reactive dye usage is responsible for by far the greatest consumption of added inorganic electrolyte in dyeing cotton.

An estimation of the scale of inorganic electrolyte usage in dyeing cotton is presented in Table 12 which is based on the assumptions that 75% (= ~19.1 × 10^6 T) of the ~ 25.5 × 10^6 T of cotton produced in 2017[44] was dyed to an average of a 2% omf depth of shade. Because, of the previously recounted reliance of inorganic electrolyte usage on liquor ratio, three values of liquor ratio are considered in Table 12, namely the currently most widely commercially utilised ratio of 1:8, a less commonly utilised BAT ratio of 1:3 and a currently commercially unavailable but nonetheless practically achievable[150,160,161] ratio of 1:1.

It is evident (Table 12) that very large amounts of NaCl, ranging from approximately 560 000 T to 4 470 000 T, may likely have been consumed in dyeing the ~19 130 000 T of cotton which it can be estimated would have been dyed in 2017 using the five types of dye/dye precursor. It is also evident that the amount of NaCl utilised in dyeing decreases markedly with decreasing liquor ratio: adopting a 1:3 liquor ratio rather than a 1:8 ratio reduces total NaCl usage by ~62%, resulting in a saving of over a little under three million tonnes of electrolyte whilst the implementation of a currently not commercially-available liquor ratio of 1:1 would reduce NaCl usage by approximately four million tonnes corresponding to a ~87% saving.

The reason why such different amounts of NaCl are required for each of the three liquor ratios considered in Table 12 is, as mentioned, because the promotional effect imparted by the inorganic electrolyte in the aqueous dyebath is strictly concentration-dependent, which means that NaCl usage increases, in-line, with the amount of water utilised for dyeing.

In the latter context, Table 12 also presents an estimate of the amounts of water that may have been consumed in dyeing cotton using each of the five classes of dye in 2017. Whilst the value of 153 000 000 T of water consumed (column seven in Table 12) was calculated assuming a 1:8 liquor ratio had been used for dyeing, concurs with the lowest value of water usage reported for a typical dyeing stage involved in cotton wet processing, as displayed in Table 6 [149] which also corresponded to a 1:8 liquor ratio, this particular level of water usage (ie 153 000 000 T) pales into insignificance in the case of the highest liquor ratio reported for a typical dyeing stage involved in cotton wet processing (Table 6),[149] namely 1:300, which would correspond to an eye watering level of water usage of 5 739 000 000 T!

As previously recounted, the reason for the very high level of reported water usage in cotton dyeing, which corresponds to an overall liquor ratio of 1:300 (Table 6), reflects cumulative water usage. In the latter context, the values of water consumption presented in Table 12 do not take into account water usage in ancillary wet processes, such as rinsing/washing, etc., associated with the 1:8 liquor ratio dyeing stage. As such, when compared to levels of water consumption typically realised in commercial cotton dyeing, such as those estimated in the case of a 1:8 liquor ratio in Table 6, the values of water consumption listed in Table 12 can be considered as being somewhat overly prudent, as they reflect only the

TABLE 12 Estimated usage of sodium chloride (NaCl) and water in dyeing cotton in 2017

Dye class	Amount of NaCl used in dyeing/ g l^{-1}[a]	Amount of cotton used in dyeing/ $\times 10^6$ T[b]	Amount of NaCl used in dyeing/ $\times 10^6$ T			Amount of water used in dyeing/ $\times 10^6$ T		
			1:8 liquor ratio	1:3 liquor ratio	1:1 liquor ratio	1:8 liquor ratio	1:3 liquor ratio	1:1 liquor ratio
Vat	5	2.49	0.09	0.04	0.01	19.89	7.46	2.49
Sulphur	5	2.49	0.09	0.04	0.01	19.89	7.46	2.49
Azoic colourant	10	1.91	0.15	0.06	0.02	15.30	5.74	1.91
Direct	5	2.10	0.08	0.03	0.01	16.83	6.31	2.10
Reactive	50	10.14	4.05	1.52	0.51	81.09	30.41	10.14
Total		**19.13**	**4.47**	**1.68**	**0.56**	**153.00**	**57.38**	**19.13**

[a]Typical amount of NaCl required for 2% omf depth of shade.

[b]Quantity of cotton dyed based on estimated consumption of different dye classes for cellulosic fibres[131] displayed in Figure 3, assuming 75% (= ~19.1 × 10^6 T) of the 25.5 × 10^6 T of cotton produced in 2017[44] was dyed.

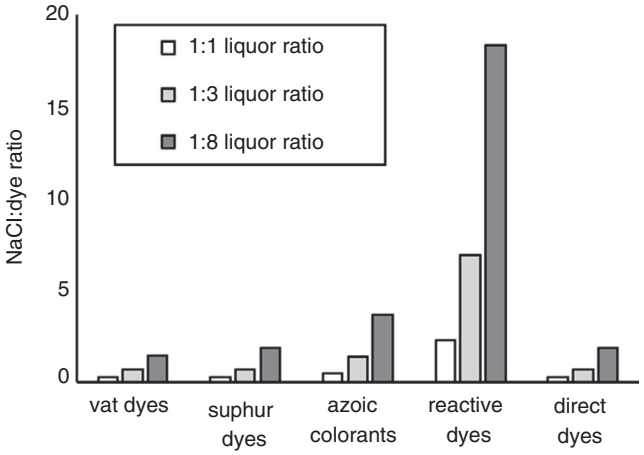


FIGURE 7 Ratio of the amount of NaCl used in dyeing cotton:/ amount of dye used in dyeing, calculated using NaCl usage in Table 12, dye usage in Figure 4[131] and assuming that 75% of the 25.5 × 10^6 Tof cotton produced in 2017[44] was dyed

lower probable levels of water usage typically encountered in cotton dyeing.

Table 12 also reveals that by far the greatest NaCl consumption occurred in the application of reactive dyes to cotton. The reasons for this are that reactive dyes characteristically require a higher concentration of inorganic electrolyte in the dyebath than their four dye/dye precursor counterparts (Table 11) and, also, because the proportion of reactive dye used on cotton is greater than that of the four remaining types of dye/dye precursor combined (Figure 3). In this context, the marked dependency of reactive dye application on both NaCl usage and liquor ratio is illustrated by Figure 7, which shows values of the ratio of the amount of NaCl used in dyeing cotton/amount of dye used in dyeing cotton, for each of the five types of dye/dye precursor.

The facts that different NaCl/dye ratios apply for the five types of dye (Figure 7) and that excessively high ratios are required for reactive dyes are considered in the second part of the article.

3 | CONCLUSIONS

From the earlier accounts of the fundamental properties and characteristics of both natural and man-made cellulosic fibres, vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes, as well as the essential principles involved in the application of each of the five classes of dye to cellulosic fibres, it is apparent that several distinctive features of the anionic dye/dye precursor/inorganic electrolyte/cellulosic fibre dyeing system merit mention:

1. cellulosic fibres are hygroscopic and adsorb appreciable amounts of water;

2. significant levels of water-induced fibre swelling and fibre plasticisation occur which ensure that the water-swollen cellulosic substrates display very low values of wet T_g;
3. the combined effects of appreciable water sorption, water swelling and low T_g enable several classes of dye to be applied to cellulosic fibres at low temperatures;
4. each of the five classes of dye is applied in the form of a highly water-soluble, dye/dye precursor anion, namely phenolate (azoic coupling component), enolate (vat dyes), thiolate (sulphur dyes) or sulphonate (direct dyes and reactive dyes);
5. the relative solubility of the different dye/dye precursor anions in the dyebath likely varies in the order: azoic coupling components = vat dyes > reactive dyes > sulphur dyes > direct dyes;
6. the amount of NaCl or Na_2SO_4 utilised in dyeing varies for each of the different classes of dye when applied to the same type of cellulosic fibre in the general order: reactive dyes >> azoic coupling components > vat dyes = sulphur dyes = direct dyes;
7. the amount of inorganic electrolyte utilised in exhaust dyeing increases with increasing liquor ratio which corresponds to an increase in the amount of dyebath water in which the dye anions are dissolved;
8. at the end of dyeing, the dye is present in the dyed substrate in the form of low solubility/insoluble/covalently bound species via regeneration/conversion/covalent reaction.

The above list and the foregoing discussion of the physicochemical aspects of the anionic dye/dye precursor/inorganic electrolyte/cellulosic fibre dyeing system suggest that the immersion application of vat dyes, sulphur dyes, azoic colourants, direct dyes and reactive dyes to cellulosic fibres is dominated by water, in terms of the effects of this unique solvent on both the physical characteristics of the cellulosic fibre and the solubility of the dye/dye precursor anion. Indeed, the high solubility of the phenolate, enolate, etc. derivative means that the high solubility dye/dye precursor anion is able to readily penetrate the wetted, water-swollen, amorphous domains of the cellulose macromolecule and associate with available -OH groups located on the cellulose macromolecular chains. However, in order for the ensuing dyed material to display satisfactory levels of durability, wet fastness, etc., the high solubility of the adsorbed dye anion has to be nullified by means of regeneration/conversion/reaction in the later stage of dyeing, so that the dye is present within the dyed substrate in the form of low solubility/insoluble/covalently bound species.

As it is well-known that each of the five classes of dye display an innate tendency to self-associate, it is likely that aggregation plays a major role in determining the characteristic features (eg fastness, hue, etc.) of the final vat dye, azoic colourant, sulphur dye, etc. dyeing. Because of the consequent dominant role that water assumes in cellulosic fibre dyeing, coupled with the fact that, as discussed in the next part of the article, such dye aggregation is encouraged in the presence of inorganic electrolyte, it follows that the likely role for added NaCl or Na_2SO_4 in cellulosic fibre dyeing may well be linked to the intrinsic high solubility of the dye/dye precursor anion in the dyebath phase.

However, this particular mechanistic explanation of the manner by which added inorganic promotes dye uptake on cellulosic fibres is only one of many theories/hypotheses/concepts that have been proposed to explain the highly complex role of added inorganic electrolyte in cellulosic fibre dyeing. As such, in order to try and identify the precise manner by which added inorganic promotes dye uptake on cellulosic fibres will require detailed consideration of these theories/hypotheses/concepts; this is the subject of the next part of the article.

REFERENCES

1. Hanson J, Neale SM, Stringfellow WA. The absorption of dyestuffs by cellulose. Part VI. The effect of modification of the cellulose, and a theory of the electrolyte effect. *Trans Faraday Soc*. 1935;31:1718-1730.
2. Geake A. The absorption of the two vat dyes Caledon Red BN and Caledon Jade Green by cotton. *J Text Inst Transactions*. 1949;40(1):T57-T87.
3. Holkar CR, Jadhav AJ, Pinjari DV, Mahamuni NM, Pandit AB. A critical review on textile wastewater treatments: possible approaches. *J Environ Manage*. 2016;182:351-366.
4. Wong JKH, Tan HK, Lau SY, Yap P-S, Danquah MK. Potential and challenges of enzyme incorporated nanotechnology in dye wastewater treatment: a review. *J Environ Chem Eng*. 2019;7(4):103261.
5. Hassan MM, Carr CM. A critical review on recent advancements of the removal of reactive dyes from dyehouse effluent by ion-exchange adsorbents. *Chemosphere*. 2018;209:201-219.
6. Katheresan V, Kansedo J, Lau SY. Efficiency of various recent wastewater dye removal methods: a review. *J Environ Chem Eng*. 2018;6(4):4676-4697.
7. Bhatia D, Sharma NR, Singh J, Kanwar RS. Biological methods for textile dye removal from wastewater: a review. *Crit Rev Environ Sci Technol*. 2017;47(19):1836-1876.
8. Nguyen TA, Juang R-S. Treatment of waters and wastewaters containing sulfur dyes: a review. *Chem Eng J*. 2013;219:109-117.
9. Singh K, Arora S. Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. *Crit Rev Environ Sci Technol*. 2011;41(9):807-878.
10. Vishnu G, Palanisamy S, Joseph K. Assessment of fieldscale zero liquid discharge treatment systems for recovery of water and salt from textile effluents. *J Clean Prod*. 2008;16(10):1081-1089.
11. Rajkumar AS, Nagan S. Study on the quality of effluent discharge by the Tirupur textile dyeing units and its impact on River Noyyal, Tamil Nadu (India). *J Environ Sci Eng*. 2010;52(4):335-342.
12. Patterson P. Eco-efficiency of Indian Dyehouses: Defra Sustainable Clothing Roadmap. London, UK: DEFRA; 2010. Accessed 06/06/20 http://sciencesearch.defra.gov.uk/Defau

lt.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=14601
13. Rajamanickam R, Nagan S. Impact of textile dyeing industries effluent on groundwater quality in Karur Amaravathi river basin, Tamil Nadu (India) - a field study. *J Environ Sci Eng*. 2010;52(4):315-320.
14. Praveen PJ. Closure of Tirupur dyeing units hits salt traders in Titucorn. The Hindu; 2011; accessed 28-04-15. http://wwwthehinducom/todays-paper/tp-national/tp-tamilnadu/closure-of-tirupur-dyeing-units-hits-salt-traders-in-tuticorin/article1771915ece
15. Prabha S, Kumar M, Kumar A, Das P, Ramanathan AL. Impact assessment of textile effluent on groundwater quality in the vicinity of Tirupur industrial area, Southern India. *Environ Earth Sci*. 2013;70(7):3015-3022.
16. Valeur CC. *The Potential for Green Textile Sourcing from Tirupur: – On the Path to More Sustainable Global Textile Chains*. Copenhagen, Denmark: Nordic Council of Ministers; 2013.
17. ANON. Reverse osmosis and ion exchange go hand in hand: textile dyeing without effluent. *Membr Technol*. 2017;2017(4):9-10.
18. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 1 an overview. *Dyes Pigm*. 2019;161:519-530.
19. Burkinshaw SM. *Physico-Chemical Aspects of Textile Coloration*. Chichester, UK: Wiley; 2016.
20. Eisenberg D, Kauzmann W. *The Structure and Properties of Water*. Oxford, UK: Plenum Press; 1969.
21. Franks F. Water: a comprehensive treatise. In Franks F (ed). *The Physics and Physical Chemistry of Water*, Vol. 1. New York, NY: Springer; 1995.
22. Franks F. *Water: a Matrix of Life*, 2nd edn. Cambridge, UK: Royal Society of Chemistry; 2000.
23. Chen B, Ivanov I, Klein ML, Parrinello M. Hydrogen bonding in water. *Phys Rev Lett*. 2003;91(21):215503.
24. Franks F, ed. *Water Science Reviews*, vol. 3. Cambridge, UK: Cambridge University Press; 2005.
25. George M. Liquid water and ices: understanding the structure and physical properties. *J Phys Condens Matter*. 2009;21(28):283101.
26. Bagchi B. *Water in Biological and Chemical Processes: From Structure and Dynamics to Function*. Cambridge, UK: Cambridge University Press; 2013.
27. Kirkham MB. Structure and properties of water. In: Kirkham MB, ed. *Principles of Soil and Plant Water Relations*, 2nd edn. Boston, MA: Academic Press; 2014:27-40.
28. Pang X-F. *Water: Molecular Structure and Properties*. Hackensack, NJ: World Scientific; 2014.
29. Rattee ID. The role of water in dyeing. *J Soc Dyers Colour*. 1974;90(10):367-372.
30. Hori T, Zollinger H. The role of water in the dyeing process. *Textile Chem Color*. 1986;18(10):19-25.
31. Burdett BC. The influence of fibre structure on dyeing. In Bird CL and Boston WS (eds). *Theory of Coloration of Textiles*. Bradford, UK: Society of Dyers and Colourists; 1975:111-162.
32. Morton WE, Hearle JWS. *Physical Properties of Textile Fibres*, 4th edn. Cambridge, UK: Woodhead; 2008.
33. Ingamells WC. The influence of fibre structure on dyeing. In: Johnson A, ed. *Theory of Coloration of Textiles*, 2nd edn. Bradford, UK: Society of Dyers and Coloursits; 1989:169-254.
34. Sun Z, Pan N. Thermal conduction and moisture diffusion in fibrous materials. In: Pan N, Gibson P, eds. *Thermal and Moisture Transport in Fibrous Materials*. Boca Raton, FL: CRC; 2006:225-270.
35. Zeronian SH. Chapter 6: Analysis of the interaction between water and textiles. In: Weaver WJ, editor. *Analytical Methods for a Textile Laboratory. Cullosics Dyeing*. Raleigh, NC: American Association of Textile Chemists and Colourists; 1984.
36. King G. Two- or three-phase adsorption theories. In: Hearle JWS, Peters RH, eds. *Moisture in Textiles*. Manchester, UK: Textile Institute; 1960.
37. Shore J, ed. *Cellulosics Dyeing*. Bradford, UK: Society of Dyers and Colourists; 1995.
38. Franck RE, ed. *Bast and Other Plant Fibres*. Cambridge, UK: Woodhead; 2005.
39. Kotek R. Regenerated cellulose fibres. In: Lewin M, ed. *Handbook of Fiber Chemistry*, 3rd edn. Boca Raton, FL: Taylor & Francis; 2007:557-772.
40. Koslowski HJ, editor. *Handbook of Natural Fibres: volume 2 Processing and Applications*. Cambridge, UK: Woodhead; 2012.
41. Koslowski HJ, editor. *Handbook of Natural Fibres: Volume 1 Types, Properties and Factors Affecting Breeding and Cultivation*. Cambridge, UK: Woodhead; 2012.
42. Turbak A. Other processes. In: Woodings C, ed. *Regenerated Cellulose Fibers*. Cambridge, UK: Woodhead; 2002:174-198.
43. BISFA. *Terminology of Man-Made Fibres*. Brussels, Belgium: BISFA; 2009.
44. Anon. Textile Outlook International No 191; 2018.
45. Woodings NS. Rayon and acetate fibres. In: Hearle JWS, Peters RH, eds. *Fibre Structure*. Manchester, UK: Textile Institute; 1963:455-479.
46. Fukuda M. Cellulosic materials (moisture sorption properties). In: Salamone JC, ed. *Polymeric Materials Encyclopedia*, vol. 2. Boca Raton, FL: CRC; 1996:1128-1135.
47. Krassig HA. *Cellulose: Structure, Accessibility, and Reactivity*. Philadelphia, PA: Gordoan and Breach Science; 1993.
48. Hearle JWS. Physical structure and fibre properties. In: Woodings C, ed. *Regenerated cellulose fibres*. Cambridge, UK: Woodhead; 2001:199-234.
49. Woodings C. Cellulose fibers, regenerated. In: Mark HF, ed. *Encyclopedia of Polymer Science and Technology*. New York, NY: Wiley; 2002.
50. Zugenmaier P. Characteristics of cellulose acetates: characterization and physical properties of cellulose acetates. *Macromol Symp*. 2004;208(1):81-166.
51. Kamide K. *Cellulose and Cellulose Derivatives: Molecular Characterization and its Applications*. New York, NY: Elsevier; 2005.
52. Perez S, Mazeau K. Conformations, structures, and morphologies of celluloses. In: Dumitriu S, ed. *Polysaccharides: Structural Diversity and Functional Versatility*, 2nd edn. New York, NY: Maecel Dekker; 2005.
53. Fang DD, ed. *Cotton Fiber: Physics, Chemistry and Biology*. Cham: Springer; 2018.
54. Wakelyn PJ, Bertoniere NR, French AD, et al. Cotton fibers. In: Lewin M, ed. *Handbook of Fiber Chemistry*, 3rd edn. Boca Raton, FL: Taylor & Francis; 2007:521-666.
55. Chanzy H. The continuing debate over the structure of cellulose: historical perspective and outlook. *Cellulose*. 2011;18(4):853-856.
56. Giles CH. The coloration of synthetic polymers: a review of the chemistry of dyeing of hydrophobic fibres. *Br Polym J*. 1971;3(6):279-290.

57. Peters RH. *Textile Chemistry*, vol. 3. Amsterdam, the Netherlands: Elsevier; 1975.
58. Nunn DM. *The Dyeing of Synthetic-Polymer and Acetate Fibres*. Bradford, UK: Society of Dyers and Colourists; 1979.
59. Steinmann HW. Cellulose acetate and fibers. In: Lewin M, Pearce EM, eds. *Handbook of Fiber Science and Technology: Volume 4: Fiber Chemistry*. New York, NY: Marcel Dekker; 1985:1001-1078.
60. Johnson A, ed. *The Theory of Coloration of Textiles*, 2nd edn. Bradford, UK: Society of Dyers and Colourists; 1989.
61. Burkinshaw SM. The application of dyes in the chemistry and application of dyes. In: Hallas G, Waring D, eds. *The Chemistry and Application of Dyes*. New York, NY: Plenum; 1990:237-380.
62. Hearle JWS, Woodings C. Fibres related to cellulose. In: Woodings C, ed. *Regenerated Cellulose Fibres*. Cambridge, UK: Woodhead; 2000:156-173.
63. Wada M, Nishiyama Y, Chanzy H, Forsyth T, Langan P. The structure of celluloses. *Powder Diffr*. 2008;23(2):92-95.
64. Gross AS, Chu J-W. On the molecular origins of biomass recalcitrance: the interaction network and solvation structures of cellulose microfibrils. *J Phys Chem B*. 2010;114(42):13333-13341.
65. Uto T, Mawatari S, Yui T. Theoretical study of the structural stability of molecular chain sheet models of cellulose crystal allomorphs. *J Phys Chem B*. 2014;118(31):9313-9321.
66. Uto T, Yui T. DFT Optimization of isolated molecular chain sheet models constituting native cellulose crystal structures. *ACS Omega*. 2018;3(7):8050-8058.
67. Kubicki JD, Yang H, Sawada D, O'Neill H, Oehme D, Cosgrove D. The shape of native plant cellulose microfibrils. *Sci Rep*. 2018;8(1):13983.
68. Jarvis MC. Structure of native cellulose microfibrils, the starting point for nanocellulose manufacture. *Philos Trans Royal Soc A: Math Phys Eng Sci*. 2018;376(2112):20170045.
69. Neale SM, Stringfellow WA. Note upon the absorption of substantive dyes by oxycelluloses of the acidic type. *J Soc Dyers Colour*. 1940;56(1):241-245.
70. Sumner HH. The mechanism of dyeing with procion dyes I—the mechanism of alkali adsorption by cellulose. *J Soc Dyers Colour*. 1960;76(12):672-678.
71. Krässig H, Schurz J, Steadman RG, Schliefer K, Albrecht W, Mohring M, Schlosser H. Cellulose. *Ullmann's Encyclopedia of Industrial Chemistry*. New York, NY: Wiley; 2000.
72. Bredereck K, Hermanutz F. Man–made cellulosics. *Rev Prog Color Relat Top*. 2005;35(1):59-75.
73. Fras L, Laine J, Stenius P, Stana-Kleinschek K, Ribitsch V, Doleček V. Determination of dissociable groups in natural and regenerated cellulose fibers by different titration methods. *J Appl Polym Sci*. 2004;92(5):3186-3195.
74. Coseri S, Biliuta G, Simionescu BC, Stana-Kleinschek K, Ribitsch V, Harabagiu V. Oxidized cellulose—Survey of the most recent achievements. *Carbohyd Polym*. 2013;93(1):207-215.
75. Motomura H, Bae S-H, Morita Z. Dissociation of hydroxyl groups of cellulose at low ionic strengths. *Dyes Pigm*. 1998;39(4):243-258.
76. Šauperl O, Stana-Kleinschek K. Differences between cotton and viscose fibers crosslinked with BTCA. *Text Res J*. 2010;80(4):383-392.
77. Neale SM, Standring PT. The measurement of donnan potentials with cellulose and aqueous solutions. *Proc Roy Soc A Math Phys Sci*. 1952;213(1115):530-545.
78. Fras LZ, Persin Z, Stenius P, Kleinscheck KS. Carboxyl groups in pre-treated regenerated cellulose fibres. *Cellulose*. 2008;15:681-690.
79. Fourné F. *Synthetic fibres: Machines and equipment, manufacture, properties*. Munich: Hanser; 1999.
80. Brandup J, Immergut EH, Grulke EA, Abe A, Bloch DR. *Polymer Handbook*, 4th edn. New York, NY: Wiley; 1998.
81. Atalla RH, VanderHart DL. Native cellulose: a composite of two distinct crystalline forms. *Science*. 1984;223(4633):283-285.
82. VanderHart DL, Atalla RH. Studies of microstructure in native celluloses using solid-state carbon-13 NMR. *Macromolecules*. 1984;17(8):1465-1472.
83. Zugenmaier P. Conformation and packing of various crystalline cellulose fibers. *Prog Polym Sci*. 2001;26(9):1341-1417.
84. LaNieve HL. Cellulose acetate and triacetate fibers. In: Lewin M, ed. *Handbook of Fiber Chemistry*, 3rd edn. Boca Raton, FL: Taylor & Francis; 2007:773-810.
85. Zugenmaier P. *Crystalline Cellulose and Derivatives - Characterisation and Structures*. Berlin, Germany: Springer; 2008.
86. Perez S, Samain D. Structure and engineering of celluloses. In: Horton D, ed. *Advances in Carbohydrate Chemistry and Biochemistry*. Volume 64. Amsterdam: Academic Press; 2010: 25-116.
87. Atalla RH, Isogai A. Celluloses. In: Liu H-W, Mander L, eds. *Comprehensive Natural Products II*. Oxford, UK: Elsevier; 2010:493-539.
88. Hearle JWS, et al. Textile fibers: a comparative overview. In: Buschow KHJ, Cahn RW, Flemings MC, Ilschner B, Kramer EJ, Mahajan S, eds. *Encyclopedia of Materials: Science and Technology*, 2nd edn. Oxford, UK: Elsevier; 2001:9100-9116.
89. Hearle JWS, et al. Textile fibers: a comparative overview. In: Buschow KHJ, Cahn RW, Flemings MC, Ilschner B, Kramer EJ, Mahajan S, eds. *Encyclopedia of Materials - Science and Technology*, 2nd edn. Oxford, UK: Elsevier; 2001:9100-9116.
90. Rowland SP, Bertoniere NR. Chemical methods of study in supramolecular structure. In: Nevell TP, Zeronian SH, eds. *Cellulose Chemistry and its Applications*. Chichester, UK: Ellis Horwood; 1985:112-137.
91. Zeronian HS, Bertoniere NR. The structures of cellulose. In: Atalla RH, ed. *Chemical Characterisation of Cellulose*. Washington, DC: American Chemical Society; 1987:255-271. ACS Symposium Series 340
92. Nevell TP. Structure of cotton in relation to dyeing. In: Shore J, ed. *Cellulosics Dyeing*. Bradford, UK: Society of Dyers and Colourists; 1995:1-80.
93. Kreze T, Stana-Kleinschek K, Ribitsch V. The sorption behaviour of cellulose fibres. *Lenzinger Ber*. 2001;80:28-33.
94. Molyneux P. Synthetic polymers. In: Franks F, ed. *Water: A Comprehensive Treatment Volume 4 Aqueous Solutions of Amphiphiles and Macromolecules*. New York, NY: Plenum; 1975:560-757.
95. Hailwood AJ, Horrobin S. Absorption of water by polymers: analysis in terms of a simple model. *Trans Faraday Soc*. 1946;42:B084-B092.
96. Peirce FT. A two phase theory of the absorption of water vapour by cotton cellulose. *J Textile Inst Trans*. 1929;20(6):T133-T150.
97. Preston JM, Nimkar MV. Measuring the swelling of fibres in water. *J Textile Inst Proc*. 1949;40(7):P674-P688.

98. Rouette H-K. *Encyclopedia of Textile Finishing*. Cambridge, UK: Woodhead; 2001.
99. Salmen NL, Back EL. The influence of water on the glass transition temperature of cellulose. *TAPPI*. 1977;60(12):137-140.
100. Batzer H, Kreibich U. Influence of water on thermal transitions in nartural polymers and synthetic polyamides. *Polym Bull*. 1981;5:585-590.
101. Steendam R, Frijlink HW, Lerk CF. Plasticisation of amylodextrin by moisture. Consequences for compaction behaviour and tablet properties. *Eur J Pharm Sci*. 2001;14(3):245-254.
102. Szcześniak L, Rachocki A, Tritt-Goc J. Glass transition temperature and thermal decomposition of cellulose powder. *Cellulose*. 2008;15(3):445-451.
103. Lindman B, Medronho B, Alves L, Costa C, Edlund H, Norgren M. The relevance of structural features of cellulose and its interactions to dissolution, regeneration, gelation and plasticization phenomena. *Phys Chem Chem Phys*. 2017;19(35):23704-23718.
104. Fuzek JF. Glass transition temperature of wet fibres. In: Rowland SP, ed. *Water in Polymers*. Washington, DC: American Chemical Society; 1980:515-530.
105. Bishop DP. Physical and chemical effects of domestic laundering processes. In: Carr CM, ed. *Chemistry of the Textiles Industry*. London, UK: Blackie Academic and Professional; 1995:125-172.
106. Urquhart AR, Eckersall N. 13—THE Adsorption of water by rayon. *J Textile Inst Trans*. 1932;23(8):T163-T170.
107. Urquhart AR, Eckersall N. The moisture relations of cotton VII a study of hysteresis. *J Textile Inst Trans*. 1930;21(10):T499-T510.
108. Beever DK, Valentine L. Studies on the sorption of moisture obt polymers Part III - cellulose acetate and cellulose triacetate. *J Textile Inst Trans*. 1958;49(2):T95-T103.
109. Krassig H, Schurz J, Steadman RG, Schiliefer K, Albrecht W, Mohring M, Schlosser H. Cellulose. *Ullman's Encyclopedia of Chemical Technology*. New York, NY: Wiley; 2012.
110. Akim EL, Naimark NI, Vasil'yev BV, Fomenko BA, Ignat'eva EV, Zhegalova NN. Effect of plasticizing liquid media on the glass transition temperatures of cellulosic materials. *Polymer Sci USSR*. 1971;13(10):2522-2529.
111. Paes SS, Sun S, MacNaughtan W, et al. The glass transition and crystallization of ball milled cellulose. *Cellulose*. 2010;17(4):693-709.
112. Zeronian S. Heat-induced changes in the properties of cotton fibers. ACS Publications. 1977.
113. Bryant GM, Walker AT. Stiffness and resiliency of wet and dry fibers as a function of temperature. *Text Res J*. 1959;29(3):211-219.
114. Cockett SR, Hilton KA. *Dyeing of cellulosic fibres and related processes*. New York, NY: Associated Press; 1961.
115. Rattee ID. Reactive dyes in the coloration of cellulosic materials. *J Soc Dyers Colour*. 1969;85(1):23-31.
116. Glenz O. Application of dyes by dyeing. In: Venkataraman K, ed. *The Chemistry of Synthetic Dyes*, vol. IV. New York, NY: Academic Press; 1971:1-74.
117. Hildebrand D. Reative dyes: application and properties. In: Venkataraman K, ed. *The Chemistry of Synthetic Dyes*, vol. VI. New York, NY: Academic Press; 1972:327-449.
118. Baumgarte U. Vat dyes and their application. *Rev Prog Color Relat Top*. 1974;5(1):17-32.
119. Rosenthal P. the chemistry and application of reactive dyes — a literature review, Sept 1971–July 1975. *Rev Prog Color Relat Top*. 1976;7(1):23-34.
120. Rattee ID. Reactive dyes: physicochemical aspects of dye fixation and dye-fiber bond hydrolysis. In: Venkataraman K, ed. *The Chemistry of Synthetic Dyes*, vol. VIII. New York, NY: Academic Press; 1978:1-36.
121. Rattee ID. Reactive dyes for cellulose 1953–1983. *Rev Prog Color Relat Top*. 1984;14(1):50-57.
122. Preston C, ed. *The Dyeing of Cellulosic Fibres*. Bradford, UK: Dyers Company Publications Trust; 1986.
123. Baumgarte U. Dyeing with vat dyes. In: Preston C, ed. *The Dyeing of Cellulosic Fibres*. Bradford, uk: The Dyers Company Publications Trust; 1986:224-255.
124. Baumgarte U. Developments in vat dyes and in their application 1974–1986. *Rev Prog Color Relat Top*. 1987;17(1):29-38.
125. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 6 analysis of conventional models that describe the manner by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres. *Dyes Pigm*. 2019;161:596-604.
126. SDC. *Colour Terms and Definitions*, 2nd edn. Bradford, UK: Society of Dyers and Colourists; 1988.
127. Morris PJT, Travis AS. A history of the international dyeing industry: Colorants; 1992. (accessed 21-04/2013): http://www.colorantshistory.org/HistoryInternationalDyeIndustry.html
128. Rowe FM. The life and work of Sir William Henry Perkin. *J Soc Dyers Colour*. 1938;54(12):551-562.
129. Welham RD. The early history of the synthetic dye industry: Part 2 The Industrial History (1856–1900). *J Soc Dyers Colour*. 1963;79(3):146-152.
130. Society of Dyers and Colourists. *Colour Index Online*. Bradford, UK: Society of Dyers and Colourists; 2016. http://colour-index.com/
131. Burkinshaw SM, Salihu G. 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. *Dyes Pigm*. 2019;161:531-545.
132. Sumner HH, Vickerstaff T, Waters E. The effects of the soaping aftertreatment on vat dyeings. *J Soc Dyers Colour*. 1953;69(6):181-194.
133. Wegmann J. Effect of structure on the change in colour of vat dyes on soaping. *J Soc Dyers Colour*. 1960;76(5):282-300.
134. Burkinshaw SM, Lagonika K. Sulphur dyes on nylon 6,6. Part 3. Preliminary studies of the nature of dye-fibre interaction. *Dyes Pigm*. 2006;69(3):185-191.
135. Aspland JR. Sulphur dyes for cellulosic fibers. *Textile Chem Color*. 1970;2:229.
136. Wood WE. Sulphur dyes–1966–1976. *Rev Prog Color Relat Top*. 1976;7(1):80-84.
137. Cook CC. Aftertreatments for improving the fastness of dyes on textile fibres. *Rev Prog Color Relat Top*. 1982;12:73-89.
138. Kramrisch B. Dyeing with direct dyes. In: Preston C, ed. *The Dyeing of Cellulosic Fibres*. Bradford, UK: The Dyers Company Publications Trust; 1986:196-223.
139. Senior C. Dyeing with sulphur dyes. In: Shore J, ed. *Cullosics Dyeing*. Bradford, UK: Society of Dyers and Colourists; 1995:280-320.
140. Senior C, Clarke DA. Dyeing with sulphur dyes. In: Preston C, ed. *The Dyeing of Cellulosic Fibres*. Bradford, UK: The Dyers Company Publications Trust; 1986:256-289.
141. Shore J. Dyeing with direct dyes. In: Shore J, ed. *Cullosics Dyeing*. Bradford, UK: Society of Dyers and Colourists; 1995:152-188.

142. Burkinshaw SM. *Chemical Principles of Synthetic Fibre Dyeing*. London, UK: Chapman and Hall; 1995.
143. Baldwinson T. Classification of dyeing and printing auxiliaries by function. In: Shore J, ed. *Colorants and Auxiliaries, Volume 2: Auxiliaries*, 2nd edn. Bradford, UK: Society of Dyers and Colourists; 2002:497-759.
144. Klemm D, Phillip B, Heinze T, Heinze U, Wagenknecht W. *Comprehensive Cellulose Chemistry: Fundamentals and Analytical Methods*. Weinheim, Germany: Wiley; 1998.
145. Warwicker JO. Swelling of cotton in alkalis and acids. *J Appl Polym Sci*. 1969;13(1):41-54.
146. Hasanbeigi A, Price L. A technical review of emerging technologies for energy and water efficiency and pollution reduction in the textile industry. *J Clean Prod*. 2015;95:30-44.
147. Tr H, Wahab A. A critical review of the current water conservation practices in textile wet processing. *J Clean Prod*. 2018;198:806-819.
148. Muthu SS, ed. *Water in Textiles and Fashion*. Cambridge, UK: Woodhead; 2019.
149. Correia VM, Stephenson T, Judd SJ. Characterisation of textile wastewaters - a review. *Environ Technol*. 1994;15(10):917-929.
150. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 5 Practical aspects of the role of inorganic electrolytes in the dyeing of cellulosic fibres with direct dyes. *Dyes Pigm*. 2019;161:581-594.
151. Valko E. Textile auxiliaries in dyeing. *Rev Prog Color Relat Top*. 1972;3(1):50-62.
152. Heimann S. Textile auxilliaries: dispersing agents. *Rev Prog Color Relat Top*. 1981;11:1-8.
153. Baldwinson T. Auxiliaries associated with main dye classes. In: Shore J, ed. *Colorants and Auxiliaries, Volume 2: Auxiliaries*, 2nd edn. Bradford, UK: Society of Dyers and Colourists; 2002:813-918.
154. Baldwinson T. Functions and properties of dyeing and printing auxiliaries. In: Shore J, ed. *Colorants and Auxiliaries, Volume 2: Auxiliaries*, 2nd edn. Bradford, UK: Society of Dyers and Colourists; 2002:471-476.
155. Lacasse K, Baumann W. *Textile Chemicals: Environmental Data and Facts*. Berlin, Germany: Springer; 2004.
156. Fischer K. *Textile Auxiliaries*, 1. Introduction. New York, NY: Wiley; 2012.
157. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 3 theoretical model to describe the role of inorganic electrolytes used in dyeing cellulosic fibres with direct dyes. *Dyes Pigm*. 2019;161:546-564.
158. Burkinshaw SM, Salihu G. 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. *Dyes Pigm*. 2019;161:565-580.
159. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres. *Dyes Pigm*. 2019;161:605-613.
160. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 8 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with commercial reactive dyes. *Dyes Pigm*. 2019;161:614-627.
161. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 9 practical aspects of the role of inorganic electrolytes in dyeing cellulosic fibres with pure reactive dyes. *Dyes Pigm*. 2019;161:628-641.
162. Willis HF, Warwicker JO, Standing HA, Urquhart AR. The dyeing of cellulose with direct dyes. Part II. The absorption of chrysophenine by cellulose sheet. *Trans Faraday Soc*. 1945;41:506-541.
163. Colours TE. Application of Duractive V dyes for cellulosic fibres; https://www.dyes.co.uk/duractivedyes.html; accessed 01/06/2020.
164. Chakraborty JN. *Dyeing with Reactive H-E dye. Fundamentals and Practices in Colouration of Textiles*. New Delhi, India: Woodhead Publishing; 2014:78-87.
165. Colours TE. Application of Duractive H dyes for cellulosic fibres; https://www.dyes.co.uk/app-duractiveh.html; accessed 01/06/2020.

How to cite this article: Burkinshaw SM. The role of inorganic electrolyte (salt) in cellulosic fibre dyeing: Part 1 fundamental aspects. *Coloration Technol*. 2021;137:421–444. https://doi.org/10.1111/cote.12547