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Coloration Technology

REVIEW ARTICLE

The role of inorganic electrolyte (salt) in cellulosic fibre dyeing: Part 2 theories of how inorganic electrolyte promotes dye uptake

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Abstract

This review concerns the application of vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive 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 processes. In this part of the paper, the various theories/hypotheses/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 physico-chemical properties of the five classes of dye used and the fundamental aspects of their application.

1 | INTRODUCTION

The first part of the paper[1] reviewed the fundamental structure and properties of *natural* cellulosic fibres (e.g. cotton, ramie, flax) *regenerated man-made* cellulosic fibres (e.g. viscose (CV), modal (CLM)) and *reconstituted man-made* cellulosic fibres (e.g. lyocell (CLY)), as well as each of the five classes of dye that are used in their *exhaust* dyeing (or *immersion* dyeing), namely vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes. In addition, an overview was presented of the essential principles involved in the application of each of the five dye classes to both natural and man-made types of cellulosic fibre.

Whilst the five different classes of dye offer to the dyer the advantage of being able to produce dyeings on cellulosic fibres that fulfil a wide range of end-use requirements (e.g. fastness, brightness, cost, etc.), because the five dye classes differ markedly from the viewpoints of their structure and physico-chemical properties, so different application conditions must be utilised for each dye class.[1] Nonetheless, the five classes of dye share one very important characteristic chemical feature, namely, that each is applied to a particular type of cellulosic fibre in the form of a highly water-soluble *anion* or *dye precursor* anion in the case of azoic coupling components, insofar as, sulphur dyes and vat dyes possess *thiolate groups*, $-S^-$, and *enolate groups*, $-C-O^-$, respectively, whilst both direct and reactive dyes carry *sulfonate groups*, $-SO_3^-$ and azoic coupling components *phenolate groups*, $Ar-O^-$ Furthermore, *inorganic electrolyte*, in the guise of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4), must be added to the aqueous dyebath in order to promote dye uptake and, thereby, secure satisfactory levels of dye adsorption. Indeed, the promotional effect imparted by added inorganic electrolyte to the uptake of vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes, is conventionally viewed as an essential, crucially important and necessarily defining aspect of exhaust dyeing processes employed for cellulosic fibres.

As large amounts of NaCl or Na_2SO_4 are routinely utilised in immersion dyeing processes for cellulosic fibres, which can be of the order of 1 kg of electrolyte per kg of cellulosic fibre dyed, and, also, because cotton, CV, CLY, etc. enjoy considerable global popularity, the exhaust dyeing of cotton and other types of cellulosic fibre using vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes is fundamentally challenged on environmental grounds. Moreover, whilst the cost of the added inorganic electrolyte contributes to the expense of conventional cellulosic fibre dyeing processes, more significantly, these are relatively small compared to the substantial costs of the treatment/disposal protocols that are required to remediate the environmentally challenged, saline, residual dyeing wastewater.

As recounted in the first part of the paper,[1] although many theories/hypotheses/concepts have been proposed to

explain the mechanism by which added NaCl or Na_2SO_4 promotes the uptake of anionic dyes/dye precursors, the precise manner by which added inorganic electrolyte promotes dye uptake is a highly complex phenomena that has not been fully resolved. In essence, the various theories/hypotheses/concepts which have been proposed consider that the possible role of added NaCl or Na_2SO_4 in exhaust dyeing processes can be explained in terms one or other of three types of interaction:

1. electrolyte-water;
2. electrolyte-fibre and/or;
3. electrolyte-dye.

This part of the paper will review and critically analyse the various hypotheses/theories, etc. of the role of added inorganic electrolyte in cellulosic fibre dyeing from the viewpoint of the above three fundamentally important aspects of the anionic dye (dye precursor)/inorganic electrolyte/cellulosic fibre system. As a corollary of this exercise, a mechanistic model is proposed which enables the phenomenon to be explained both conceptually and rationally, without the need to resort to large experimental dye adsorption data generation and associated complicated mathematical data analysis.

2 | THEORIES OF THE ROLE OF INORGANIC ELECTROLYTE IN CELLULOSIC FIBRE DYEING

The majority of the manifold theories that have been proposed to account for the manner by which added NaCl or Na_2SO_4 promotes the uptake of anionic dyes/dye precursors on cotton and other types of cellulosic fibre were devised some 70-100 or so years ago to explain the promotional effects imparted to both the rate and extent of direct dye uptake on cotton and the various types of man-made cellulosic fibre then available [e.g. 2-17; see 18-24 for summaries]. This focus on the direct dye/inorganic electrolyte/cellulosic fibre system reflected both the major commercial importance of this particular dye class at the time (reactive dyes, which are nowadays the most popular dye class employed for cellulosic fibres, were not introduced until the mid-1950s) and the fact that the application of direct dyes was the most amenable of the dye classes then available to empirical investigation, as it does not present anyway near the level of inherent experimental difficulty as does that of the leuco forms of both vat dyes and sulphur dyes, and, to a lesser extent, that of alkali-solubilised, azoic coupling components.

Unfortunately, the findings of these early experimental investigations that sought to identify the role of added NaCl or Na_2SO_4 in direct dye uptake (which, characteristically, were both superbly detailed and elegantly presented), are of questionable relevance, since they routinely utilised samples of only a few, mostly purified, direct dyes (e.g. C.I Direct Blue 1, C.I Direct Yellow 12, C.I Direct Red 1), that are not representative of commercial dye products which typically contain various additives (e.g. diluents, shading dyes, etc.) incorporated by the dye maker as part of the dye manufacturing process. In the latter context, a commonly employed standardising component in commercial dye products is NaCl, which is used as a diluent to adjust *tinctorial strength* (and also is arguably the most popular inorganic electrolyte employed in cellulosic fibre dyeing). This is exemplified by the findings that three samples of commercial grade direct dyes contained differing levels of diluent NaCl, namely, C.I. Direct Blue 71: 8.3%, C.I. Direct Red 81: 9.5% and C.I. Direct Yellow 50: 6.5%,[25] whilst the amount of diluent NaCl present in three commercial grade reactive dye samples ranged from 11.5% to 12.3%.[26] Moreover, such early dyeing studies often utilised highly idealised cellulosic substrates, such as cellulose sheets, rolls, etc., which are not representative of typical cellulosic textile fibre materials (e.g. woven cotton fabrics, knitted shirting, etc.), and also routinely adopted exceptionally high liquor ratios, *LR* (e.g. 1:50, 1:100, 1:250, etc.) which bear no resemblance to those employed commercially.

Nonetheless, these innovative, pioneering early studies of the dyeing behaviour of direct dyes on cellulosic fibres are of fundamental importance as they focussed primarily on establishing the *theory of dyeing* cotton and other types of cellulosic fibre using direct dyes and, thereby, sought to determine the *mechanism* by which direct dyes are adsorbed onto cellulosic fibres and the role of inorganic electrolyte in this process. Impressively, the ground-breaking experimental protocols and systems of data analysis that were devised by these early researchers ~70-100 years ago are still utilised in contemporary investigations that seek to explore the *theory of dyeing* various types of fibre (e.g. wool, polyamide, polyester, etc.) using various classes/types of dye (e.g. disperse dyes, non-metallised acid dyes, etc.), as expressed in terms both the *thermodynamics* and *kinetics* of dye adsorption. Indeed, these particular classic empirical investigative techniques enjoy widespread usage in many of the currently very popular studies of the remediation of dyeing wastewater by adsorption onto various types of adsorbent.[27-31]

In view of the fundamental importance and significance of the *theory of dyeing*, it seems reasonable that this review of the role of inorganic electrolyte in cellulosic fibre dyeing should commence with a discussion of the information and knowledge which the thermodynamic and kinetic analyses of anionic dye adsorption on cellulosic fibres provides.

3 | THERMODYNAMIC AND KINETIC INTERPRETATIONS OF THE ROLE OF INORGANIC ELECTROLYTE IN CELLULOSIC FIBRE DYEING

In terms of the mechanism by which added inorganic electrolyte promotes the uptake of vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes on cotton and other types of cellulosic fibre, a substantial amount of information has been published over many decades concerning both the thermodynamic and kinetic aspects of the anionic dye/inorganic electrolyte/cellulosic fibre system as, for example, described in various textbooks[18,19,22-24,32-34] and articles,[5,13,15,35-38] although such studies have tended to focus primarily on direct dyes and, to a lesser extent, reactive dyes (as mentioned, vat dyes, sulphur dyes and azoic colorants have received much less attention because of inherent experimental challenges associated with their application).

As intimated above, conventional approaches to establishing the thermodynamic basis of dye adsorption invariably utilise highly specialised dyeing conditions (e.g. purified dye, idealised substrate, isothermal dyebath, protracted dyeing times, etc.) so that *equilibrium dye adsorption* can be achieved, from which the corresponding *equilibrium dye adsorption isotherm* can be constructed. This then allows one or other *mathematical model* to be devised that provides some or other perceived level of concurrence with the experimentally observed data and which can be used to provide the basis upon which a *theory* can be proposed to explain the mechanism by which dye adsorption proceeds. Typical results obtained from such conventional thermodynamic studies of the effect of NaCl on direct dye adsorption are presented in Figure 1 where $[D]_f$ is the amount of dye present in the fibre relative to the amount of fibre and $[D]_s$ the amount of dye in solution (i.e. the external dyebath) relative to the amount of solution.

Unfortunately, conventional thermodynamic analyses of aqueous dyeing processes are fundamentally unable to explain *why* the inorganic electrolyte that is added to aqueous direct dye, etc., dyebaths, increases dye uptake. This is simply because, in essence, studies that seek to establish the thermodynamic basis of dye adsorption are *quantitative research tools* which are intrinsically designed to:

1. investigate the experimentally observable empirical phenomena of anionic dye adsorption and the effect of added NaCl or Na_2SO_4 on dye uptake, commonly via the use of equilibrium dye adsorption isotherms in the guise of those displayed in Figure 1, and;
2. devise a mathematical equation which provides some level of fit to the experimentally obtained dye adsorption data, which can then be used to support a particular theory/hypothesis/model that describes the experimentally observed anionic dye/inorganic electrolyte/cellulosic fibre phenomena.

Consequently, studies of the thermodynamics of dyeing can only *observe* and *quantify* the promotional effects which added inorganic electrolyte impart to dye uptake, as demonstrated by the data presented in Figure 1. However, the various derivatised mathematical expressions that have been formulated to explain the experimental results obtained in such dyeing studies (and thereby support a particular theory/hypothesis of dyeing), nevertheless invariably assume or presume a role for the inorganic electrolyte in the dyeing process and, in so doing, surmise a possible mechanism by which added NaCl or Na_2SO_4 promotes dye uptake.

Indeed, conventional theories of direct dye adsorption are based on the fundamental assumption that a *negative electrical charge* is present at the cellulosic fibre-water interface and that the adsorption of direct dye anions increases the magnitude of this surface charge.[23,24,34] Of the various theories and hypotheses reviewed in sections 4 to 6 that have been suggested to account for the promotional effect of added inorganic electrolyte on direct dye uptake (and that of the other four types dye/dye precursor) on cellulosic fibres, by far the most commonly cited is that which postulates that Na^+ cations derived from the added NaCl of Na_2SO_4, *neutralise* the negative charge that is present at the surface of solvated cellulosic fibres, which thereby reduces electrostatic repulsion operating between the adsorbing direct dye anions (i.e. D-SO_{3^-}) and the negatively charged fibre surface that accrues from the presence of ionised carboxyl groups, Cell-COO^- and also, depending on pH, ionised hydroxyl groups, Cell-O^-, which promotes dye uptake. The pH-dependency of both the -COOH and -OH groups in cellulose is discussed in section 5.

As such, the most popular theory/hypothesis used to explain the role of inorganic electrolyte in cellulosic dyeing is therefore directly and intrinsically linked to the most fundamental assumption employed in thermodynamic models

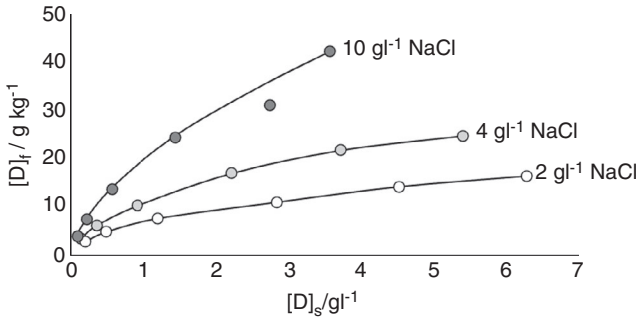

FIGURE 1 Equilibrium adsorption isotherms for purified C.I Direct Yellow 12 on cellophane (CV) sheet at 60°C showing the effect of increasing amounts of NaCl on dye uptake; drawn using data from[8]

of direct dye adsorption namely, the presence of a negative charge at the cellulosic fibre-water interface. However, as also discussed in section 5, whilst the notion that inorganic electrolyte-derived Na^+ cations neutralise the negative fibre surface charge conveniently links theories of dye adsorption to the role of added NaCl or Na_2SO_4, the experimental evidence to support this linkage is, at best, unconvincing.

Moreover, as articulated in section 3.1, conventional thermodynamic analyses of the anionic dye/inorganic electrolyte/cellulosic fibre system leave much to be desired, simply because the correlation between the experimentally observed promotional effects exerted by inorganic electrolyte on dye uptake, such as those illustrated in Figure 1, and the various mathematical expressions which have been devised to interpret this empirically observed data, is at best, ambiguous. Indeed, none of the mathematical models that have been proposed over the last ~80 or so years is able to satisfactorily account for the promotional effect exerted by added inorganic electrolyte on dye uptake; inconsistencies are invariably observed between theoretically derived equations and experimentally secured dye adsorption data.[19,22-24,34]

In addition, because experimental observation and data measurement are central precepts of quantitative research, as they intrinsically link empirical observations to the resulting, allied mathematical interpretation of those experimental observations, so the conventional thermodynamic analysis of the anionic dye/inorganic electrolyte/cellulosic fibre system is again profoundly flawed. This is simply because the highly specific, idealised and essentially unrealistic application conditions that must be employed to achieve equilibrium dye uptake bear no resemblance at all to those utilised in real (commercial) dyeing processes, which are carried out under conditions that purposefully aim to achieve complete dye uptake well before equilibrium dye adsorption is even approached, let alone achieved. Experimental equilibrium dye adsorption data therefore offers little, if any, constructive information regarding an exhaust dyeing process prior to equilibrium dye uptake being accomplished which, of course, is of crucial significance from the perspective of real immersion dyeing processes. Indeed, simply observing that added NaCl or Na_2SO_4 influences dye uptake and deriving an equation that fits the experimentally observed data, as is employed in conventional studies of the thermodynamics of dyeing, provides an intrinsically incomplete *theory of dyeing* because that particular dyeing theory does not offer the crucially important explanation of the *mechanism by which* added inorganic electrolyte influenced the extent of equilibrium dye uptake observed.

In contrast to the thermodynamics of dyeing, the *kinetic aspects* of dye adsorption typically provide information that concerns the *rate* at which a particular dye diffuses within both the aqueous dyebath phase and the (solid) fibre phase. As the kinetics of dyeing concerns the rate at which a particular dye is adsorbed by a given type of cellulosic fibre, it should in theory provide information that is more relevant to practical commercial exhaust dyeing processes which are intended to furnish dyeings within a desired, shortest time frame as possible.

Our fundamental knowledge and understanding of the diffusional behaviour of anionic dyes within cellulosic fibres from the perspective of the role of added NaCl or Na_2SO_4, as mentioned, stems from pioneering studies, initiated some 70-100 or so years ago, that focussed on the rate of direct dye uptake on cotton and the various types of man-made cellulosic fibre then available.[9,39-43] Once again, studies of the kinetics of dye adsorption are *quantitative research tools*, in that they investigate the observable, empirical phenomena of dye diffusion and the effect of added NaCl or Na_2SO_4 on dye diffusional behaviour, and typically employ mathematical models which are designed to fit the observed experimentally secured data, which can then be used to support a particular theory/hypothesis/model that describes the observed dye diffusional phenomena.

However, in a similar manner to studies of the thermodynamics of dye adsorption, experimental studies of the kinetics of anionic dye adsorption on cellulosic fibres and the effect of added inorganic electrolyte on dye diffusional behaviour tend to be carried out under very precise and, for the most part, highly restricted dyeing conditions, which typically utilise idealised substrates (e.g. cellulose polymer films, assemblies of CV sheets, etc.) in various physical forms, (e.g. roll, disc, etc.), purified dyes, very long liquor ratios, etc., as well as very well-defined application conditions referred to as *boundary conditions* (e.g. finite dyebath, short diffusion times, constant dye concentration) from the viewpoint of the subsequent mathematical interpretation of the experimental data, which are mostly unrepresentative of those encountered in real dyeing processes.

Furthermore, as the particular boundary conditions selected for study, such as *steady-state* (i.e. constant dye concentration gradient with zero rate of dye accumulation) or *non-steady-state* (i.e. non-constant dye concentration gradient and increasing dye accumulation) dyeing conditions, *substrate geometry* (e.g. cylinder, slab, film, etc.) and, indeed, *dyebath type* (i.e. *finite* or *infinite*), are often specifically chosen so that the ensuing experimental data can be interpreted using one or other type of theoretical solution to *Fick's First* or *Second Law of Diffusion*, the practical value of the information they provide is, at best, somewhat limited. Typical results obtained from kinetic studies relating to the effect of NaCl on direct dye adsorption are presented in Figure 2.

As the conventional thermodynamic and kinetic analyses of the direct dye/inorganic electrolyte/cellulosic fibre

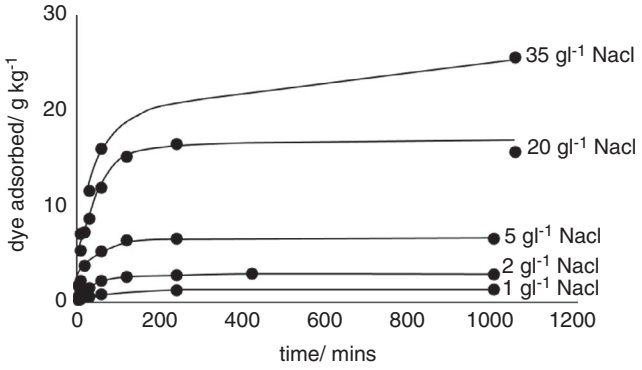

FIGURE 2 Effect of added NaCl on the rate of diffusion of purified C.I. Direct Blue 1 in cellophane sheet of thickness 0.00451 cm; 0.05 g l^{-1} dye; 1:1000 LR; 100°C; drawn using data from[39]

system[44] and reactive dye/inorganic electrolyte/cellulosic fibre system[45] were reviewed recently, and detailed general accounts are available,[18,19,22-24,32-34] the following serves as a summary.

3.1 | Thermodynamic analysis

The equilibrium adsorption of direct dyes onto cellulosic substrates is commonly interpreted using a *Freundlich-type* isotherm equation according to which, the initial stages of the characteristically sigmoidal-shaped dye adsorption isotherm plots, such as those depicted in Figure 1, corresponds to the formation of *monolayers* of adsorbed, monomolecular dye anions which are associated with non-specific adsorption sites located on cellulose chains within the water-swollen, amorphous domains in the cellulosic material. Subsequent adsorption involves the formation of *multilayers* of adsorbed dye molecules associated with non-specific sites located within the amorphous regions in the substrate.

Such *multilayer adsorption* is indicative of that of *dye aggregates* at non-specific sites,[22] which is to be anticipated on the basis of the previously discussed[1] inherent disposition of planar direct dye molecules to engage in co-planar, self-association via π-π interactions operating between aromatic centres in neighbouring dye molecules.

In contrast, the equilibrium adsorption of direct dyes on cellulosic fibres has also been observed to correlate with a *Langmuir-type* mechanism that corresponds to the formation of a *monolayer* of dye anions located at a limited number of specific, equivalent, adsorption sites within the cellulose macromolecular chains in the amorphous regions of the substrate.

However, debate attends the precise nature of the adsorption sites within the cellulose material. Whilst the obvious choice are the numerous -OH groups that are located along the cellulose macromolecular chains that reside within the amorphous domains in the cellulosic substrate, the Langmuir-type adsorption mechanism dictates that only a limited number of -OH groups will be present in the fibre that display some or other type of pronounced *selectivity* with regards the adsorbing direct dye molecules.

Thus, from the perspective of the Langmuir-type adsorption process, the cellulose polymer is assumed to contain certain types of hydroxyl group that display different adsorption character to that of other types of -OH group. Such selectivity of the hydroxyl groups towards adsorbing direct dye molecules may well reflect the well-known phenomenon that not all of the component -OH groups in cellulose polymers are equally *accessible* to water molecules and, therefore, by association, to dissolved reagents,[22,46-49] such as, in this case, dye molecules.

Briefly, each monomeric *D*-glucose unit (i.e. *anhydroglucose unit*) of the cellulose polymer chain contains one -OH group located at the C-6 position which behaves as a primary alcohol in its reactions, as well as two secondary alcoholic -OH groups located at the C-2- and C-3 positions. The -OH groups in cellulose therefore display inherently different chemical reactivity owing to their primary or secondary alcoholic behaviour. The reactions which the three -OH groups undergo are further influenced not only by the extensively H-bonded, three-dimensional network structure of cellulose, in terms of their relative involvement in *intramolecular* H-bonding between -OH groups in the same chain molecule, and *intermolecular* H-bonding between -OH groups in neighbouring macromolecular chains, but also by the *microfibrillar structure* of natural, regenerated and reconstituted cellulosic fibres, in that access of water and dissolved reagents to -OH groups located within highly ordered *elementary fibril* surfaces can be expected to be more restricted than to their counterparts which are located within less ordered elementary fibril surfaces.

Because the -OH groups in cellulose polymers are not equally accessible to water molecules, it seems reasonable to suggest that the hydroxyl groups may well display *heterogeneous reactivity* towards dissolved reagents, in this case, adsorbing dye molecules. This may go some way to explain the selectivity of the hydroxyl groups towards adsorbing direct dye molecules demanded by the Langmuir-type adsorption mechanism.

The Langmuir-type adsorption mechanism also specifically forbids any interaction between dye molecules adsorbed at neighbouring -OH group sites, which means that dye aggregation is unable to contribute towards dye uptake. This latter somewhat austere pre-requisite of the Langmuir-type adsorption process does not fit at all well with the very well-known intrinsic disposition of direct dyes to self-associate, especially in the presence of added NaCl or Na_2SO_4;[22] this latter characteristic feature of direct dyes, which also applies

to the other four classes of dye utilised on cellulosic fibres, is discussed in section 6.

As mentioned, a central tenet of the thermodynamic analysis of equilibrium dye adsorption (which, the neutral observer may well be excused for assuming is the main reason why equilibrium dye adsorption studies are undertaken), is to devise some or other mathematical model that provides some or other level of perceived correspondence with experimentally observed equilibrium dye adsorption isotherm data, which can then use to support a mechanistic theory/hypothesis of the dye adsorption process. From the perspective of the dyeing of cellulosic fibres, several such mathematical models, which accord with either Freundlich-type or Langmuir-type adsorption processes, have indeed been devised to describe the mechanism of direct dye adsorption, of which, the *diffuse adsorption model* of Marshall and Peters,[10] dating from 1947, is perhaps most widely cited.

In this particular model, as expressed in the form of Equation 1, where $-\Delta\mu^{\theta}$ represents the standard affinity of the direct dye, R the universal gas constant and T temperature (Kelvin), the direct dye/inorganic electrolyte/cellulosic fibre system is divided into two parts, namely an *external aqueous solution phase*, *s*, and an *internal solution phase*, *f*, that resides within the solvated fibre. The two phases are in equilibrium and both direct dye anions, D^{-}, of valency z (i.e. $Na_{z}D^{z-}$) and electrolyte-derived cations, Na+, are distributed across the two solution phases.

$$-\Delta\mu^{\circ} = \mathrm{RTln}\frac{[Na^{+}]_{f}^{z}[D^{-}]_{f}}{V^{z+1}[Na^{+}]_{s}^{z}[D^{-}]_{s}} \quad (1)$$

Unfortunately, whilst the amounts of adsorbed direct dye anion present in each phase can be experimentally measured, as can the sodium cation concentration in the solution phase, the concentration of the electrolyte-derived cation in the internal solution phase within the fibre (i.e. the term $[Na^{+}]_{f}^{z}$ in Equation 1) cannot be determined experimentally. Instead, the concentration of Na^{+} ions in the fibre solution phase can only be calculated, employing *Donnan membrane equilibrium theory*[22] and invoking the use of the concept of *fibre internal volume*, *V*.[22] In essence, the latter variable represents some or other cellulosic substrate-related parameter that most probably represents some or other aspect of the volume of the substrate that is accessible to the adsorbing direct dye anions.

Whilst conceptually, *what* exactly the internal volume of a cellulosic fibre is and precisely *how large* this particular volume may be, remain matters of debate, the *purpose* of this particular volumetric parameter is very clear, namely, to ensure that values of standard affinity, $-\Delta\mu^{\theta}$, calculated for a given direct dye using Equation 1 (or others like it), accord with a *presumed* theory of direct dye adsorption on *cellulose polymers* (as opposed to adsorption onto a given type of *cellulosic fibre*). By way of brief explanation, Neale,[3] the originator of the concept of *internal volume* as employed in the thermodynamic analysis of anionic dye adsorption on cellulosic fibres, proposed a value for cotton of $V = 0.22\ \mathrm{l\ kg^{-1}}$, as this particular value, which represented the amount of water sorbed by the particular sample of cotton at *saturation* (i.e. 100% Relative Humidity, *RH*), gave the best mathematical fit to equilibrium adsorption isotherm data obtained for purified C.I. Direct Blue 1 on cotton.

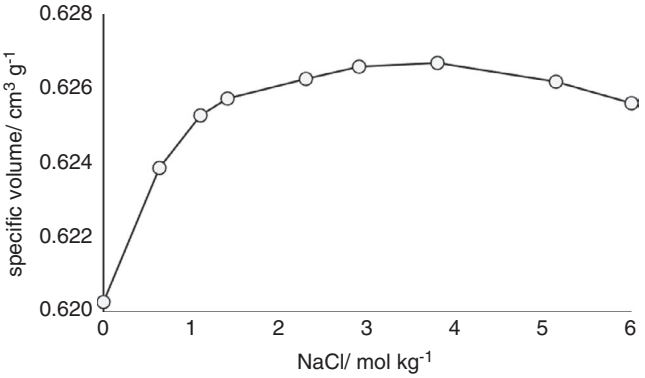

FIGURE 3 Effect of sorbed NaCl on the specific volume of CV sheet at 25°C; drawn using data from[16]

However, as different types of cellulosic substrate typically sorb different amounts of water at saturation (e.g. V/l kg^{-1}: cotton: 0.22; mercerised cotton 0.26; CV 0.46; cellophane sheet 0.33[23]), so different values of V may be employed in Equation 1. Unhelpfully, as might be expected from the influence of the term V in equations such as Equation 1, if different values of V are employed for the same type of fibre, for example cotton, then markedly different values of standard affinity will be secured,[23,34] which is far from satisfactory [e.g. V/l kg^{-1}: $-\Delta\mu^{\theta}$ kJ mol^{-1} 0.1: 33.8; 0.2: 24.9; 0.22: 23.8; 0.3: 20.6; C.I Direct Blue 1 on cotton at 90°C $[D]_{f} = 8.84 \times 10^{3}$ mol kg^{-1}; $[D]_{s} = 4.04 \times 10^{4}$ mol l^{-1}; $[Na]_{f} = 8.74 \times 10^{2}$ mol l^{-1}[34]].

Alternatively, some authors employ a particular arbitrary value for V that is deemed to deliver some or other optimum level of concurrence between experimentally obtained equilibrium direct dye adsorption data and a particular associated mathematical model that describes the direct dye/inorganic electrolyte/cellulosic substrate phenomena under investigation.

Interestingly, Neale subsequently demonstrated[16] that the presence of various types of adsorbed inorganic electrolyte, including NaCl, increased the *specific volume* of cellophane sheet (Figure 3), though reasons for the observed reduction in specific volume that occurred at high amounts of electrolyte were not identified. The findings that the specific volume of cellulose varied, markedly, as a function of the concentration

of inorganic electrolyte, along the lines presented in Figure 3,[16] suggest that the particular value of V that is employed in equations such as Equation 1 (and others like it) should be chosen according to the specific amount of inorganic electrolyte used for dyeing, which, curiously, is not usually the case.

For discussions of the intriguing topic of cellulosic fibre *internal volume*, see.[19,22-24,34]

Unfortunately, because the precise nature of V and, indeed that of the idiosyncratic concept of the internal volume of a cellulosic substrate, have not been fully rationalised, the agreement between theoretically derived mathematical models of dye adsorption, as illustrated by Equation 1 (and others like it) and experimentally secured, isothermal equilibrium dye adsorption data (as illustrated by that shown in Figures 1 and 4) leaves much to be desired.

This particular situation is further exacerbated by the fact that because of the intrinsically challenging nature of both the mathematical and conceptual assumptions of *Donnan Theory*, the calculation of values for $[Na^+]_f^z$ in Equation 1 is inherently problematic.[22,34] Indeed, as mentioned, from the perspective of the role of inorganic electrolyte in cellulosic fibre dyeing, such mathematical models are unable to account for the precise manner by which added NaCl or Na_2SO_4 promotes direct dye uptake. In essence, all that Equation 1 (and others like it) accomplish is to quantify the consequence of the promotional effect imparted by added inorganic electrolyte in terms of the standard affinity, $-\Delta\mu^\theta$, of the direct dye towards a particular cellulosic substrate (assuming an appropriate value of V is employed).

Such innate inadequacy of conventional thermodynamic models of direct dye adsorption is illustrated by the fact that when experimentally derived equilibrium adsorption data, which shows that direct dye adsorption increases with increasing amounts of NaCl employed (as illustrated by the results shown in Figure 4) are analysed using some

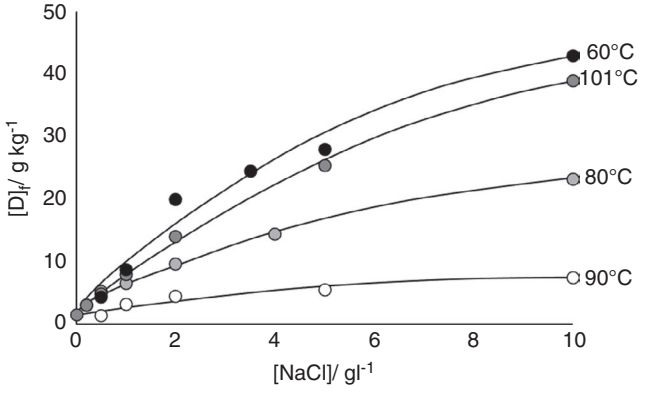

FIGURE 4 Variation of equilibrium adsorption achieved for C.I Direct Blue 1 (60°C), C.I Direct Yellow 12 (80 and 90°C) and C.I. Direct Red 2 (101°C) on CV as a function of added NaCl; drawn using data from[5,8,40,50]

mathematical model of the anionic dye/inorganic electrolyte/cellulosic fibre system, such as Equation 1, the resulting values of standard affinity do not correspond at all well to the experimentally observed variation in equilibrium dye uptake as a function of inorganic electrolyte concentration.[11,22,34] In essence, whereas calculated standard affinity values display only moderate increases as a function of increasing electrolyte concentration these do not correspond to the often sizeable experimentally observed increase in equilibrium direct dye adsorption that accompanies an increase in NaCl.

This is illustrated by the data presented in Figure 5 and by the findings that whilst a 600% increase in the concentration of added NaCl used for dyeing increased the equilibrium uptake of C.I. Direct Blue 1 on cuprammonium rayon (CUP) by >200%, the corresponding values of standard affinity, $-\Delta\mu^\theta$, increased by only 2% [i.e. $[D]_f$/g kg^{-1} @ [Na]$_f$/g l^{-1} ($-\Delta\mu^\theta$/kJ mol^{-1}): 11.3 @ 5.0 (23.8); 17.3 @ 10.0 (23.9); 26.0 @ 20.0 (24.1); 36.0 @ 35.0 (24.3); 0.058 g l^{-1} dye; 90°C; $V = 0.55$ l kg^{-1} (32)].

Moreover, according to theoretical considerations,[11,24] calculated values of standard affinity for a given direct dye/inorganic electrolyte/cellulosic substrate system should be more or less *constant* irrespective of inorganic electrolyte concentration and, therefore, they do not adequately portray typically observed variation of equilibrium dye uptake as a function of added electrolyte concentration.

Furthermore, although the early pioneering studies discussed above focussed on the role of added NaCl or Na_2SO_4 on the uptake of direct dyes on cellulosic fibres, the findings of these investigations and the consequent mechanistic implications proposed, are, in essence, tacitly presumed to apply to the other four classes of dye used on cellulosic fibres, namely vat dyes, sulphur dyes, azoic colorants and reactive dyes. For example, when what is nowadays by far the most popular class of dye used for cellulosic fibres,[44] namely reactive dyes, were introduced in the 1950s, it was assumed mechanistically from the viewpoint of the conventional thermodynamic treatment of the equilibrium adsorption of anionic dyes on cellulosic fibre, that because of the structural similarities between direct dyes and the reactive dyes available at the time, the adsorption behaviour of reactive dyes prior to the covalent attachment of the colorant to the substrate, occurs in an identical manner to that of direct dyes. Therefore, mechanistically, it is assumed that added inorganic electrolyte performs exactly the same role in both direct dye uptake and reactive dye uptake on cellulosic fibres, even though the two types of dye differ, significantly, in terms of the fundamental nature of the exhaust dyeing procedures employed for the two different classes of dye. For example, as it is well-known that added NaCl or Na_2SO_4 promotes *both* the processes of dye adsorption and *dye-fibre fixation* in the case of reactive dyes, whereas the application of direct dyes does not of course involve dye-fibre fixation, it is difficult to reconcile the

assumed notion that added inorganic electrolyte plays identical roles in the two types of exhaust dyeing process.[19,22,32,34]

A similarly unconvincing approach is adopted in the case of the thermodynamic analysis of the adsorption of the leuco form of vat dyes on cellulosic fibres. In this case, the role of added inorganic electrolyte in the application of leuco vat dye anions (i.e. Dye-C-O^-) is once again assumed to be identical to that which applies for the application of direct dye anions (i.e. Dye-SO_3^-), even though the dyebath conditions that are typically encountered in a leuco dye dyebath (e.g. high alkalinity, reducing agents, anti-oxidation conditions, etc.) are very much different to those encountered in a typical direct dye dyebath (no alkali, no reducing agents, etc.). The assumed parity of the role of added NaCl or Na_2SO_4 in the thermodynamic analysis of the adsorption of vat dyes and direct dyes on cellulosic fibres is also based on remarkably very few practical studies of vat dyeing processes (which reflects the inherent experimental challenges that leuco vat dyebaths present).

An analogous situation applies in the case of what really can only be considered as being the *presumed roles* of inorganic electrolyte in the application of both the leuco form of sulphur dyes (i.e. Dye-S^-) and alkali-solubilised azoic coupling components (i.e. Ar-O^-) to cellulosic fibres. It is once more assumed that the nature of the promotional effect exerted by added inorganic electrolyte on anionic dye/dye precursor uptake is identical to that which applies in the case of direct dyes, even though, once again, sulphur dyes and azoic coupling components are structurally very different to direct dyes and the composition of the dyebaths utilised in the application of sulphur dyes (e.g. high alkalinity, reducing agents, anti-oxidant conditions, etc.) and azoic coupling components (e.g. high alkalinity, low temperatures, etc.) differ greatly to that of dyebaths employed for their direct dye counterparts. Furthermore, these assumptions are once again based on very few experimental observations, which again can be attributed to the experimental challenges presented by the highly alkaline, multi-component, etc., composition of the leuco sulphur dye and alkali-solubilised azoic coupling component, dyebaths.

Finally, the innate differences discussed above between the nature of the direct dye adsorption processes described by the Freundlich-type and the Langmuir-type adsorption mechanisms cannot be resolved mechanistically. As to which adsorption mechanism is correct or, rather, which is perceived by a particular researcher employing a given combination of experimental materials and selected dyebath conditions as being least incorrect, will no doubt remain a subject of debate, simply because the two adsorption processes are so profoundly different in their respective presuppositions.

Whilst this situation may be attributed to our lack of understanding of several, fundamentally important, but, mostly unresolved concepts, such as those delineated in the first part of the paper[1] (e.g. the inherently complex and complicated nature of electrolyte-water, electrolyte-dye and electrolyte-cellulosic fibre interactions, together with a somewhat hazy appreciation of the precise nature of anionic dye/dye precursor-cellulosic fibre substantivity and the influence of added inorganic electrolyte on dye-fibre substantivity, etc.) a far more searching and judgemental observation can be advanced: what type of information does the thermodynamic analysis of equilibrium dye adsorption, as inferred from the findings of so many mechanistic studies of the anionic dye/

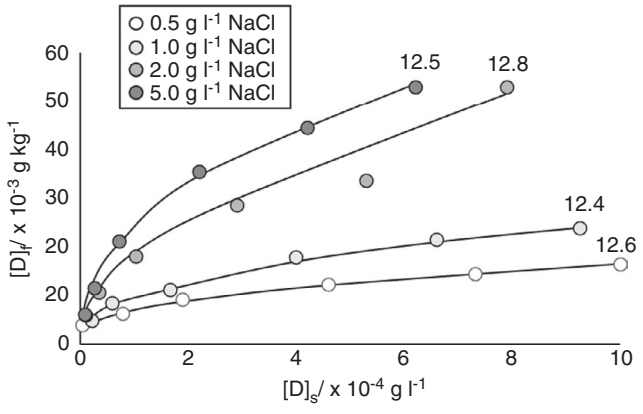

FIGURE 5 Effect of added NaCl on equilibrium adsorption of C.I Yellow 12 on CV at 40°C; figures on curves are mean values of standard affinity, $-\Delta\mu^o$/kJ mol^{-1}; drawn using data from[24]

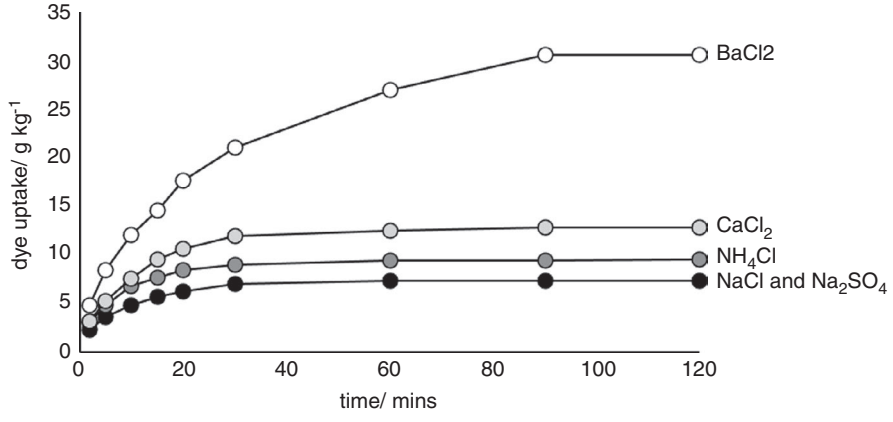

FIGURE 6 Effect of different inorganic electrolytes on the uptake of purified C.I. Direct Blue 1 on CV (0.086 M electrolyte; 0.05 g l^{-1} dye; 98°C; drawn using data from[43]

dye precursor/inorganic electrolyte/cellulosic fibre system that have been carried out over the past 70-100 or so years, *really* provide that is of relevance to the role of inorganic electrolytes in cellulosic fibre dyeing? As is perhaps apparent from the above discussion, this author is of the opinion that the answer to this elementary question is *not very much actually*.

Whilst this latter statement may appear harsh and austere, which is most definitely not the intention, and, of course, hindsight is such a wonderful but yet intriguingly unworkable concept, the statement does reflect both the inherent complexity of the anionic dye/dye precursor/inorganic electrolyte/cellulosic fibre system and the intrinsically complicated nature, and necessarily limited capability, of, conventional thermodynamic analysis of dyeing systems.

3.2 | Kinetic analysis

The general topic of the kinetics of dye adsorption has received considerable attention [see 19,22-24,33,51-54 and the references therein].

From the perspective of cellulosic fibre dyeing and the role of added NaCl or Na_2SO_4 in dye uptake, the vast majority of kinetic studies have focussed on direct dyes, as demonstrated by the results presented in Figure 6 and, to a lesser extent, reactive dyes,[36,38,39,55-63] though the kinetics of vat dye adsorption have received attention, as illustrated by the findings shown in Figure 7.

Essentially, the *kinetics of dyeing* seeks to establish the *mobility* of diffusing dye molecules within the aqueous dyebath phase and/or within the water-filled amorphous domains that reside in the water-swollen fibrous substrate. In this context, the rate at which the dye molecules diffuse through the given dyebath and/or fibre phase, which is a dye-related parameter referred to as *diffusivity*, is quantified conventionally in terms of the *diffusion coefficient*, *D*, of the dye molecules.

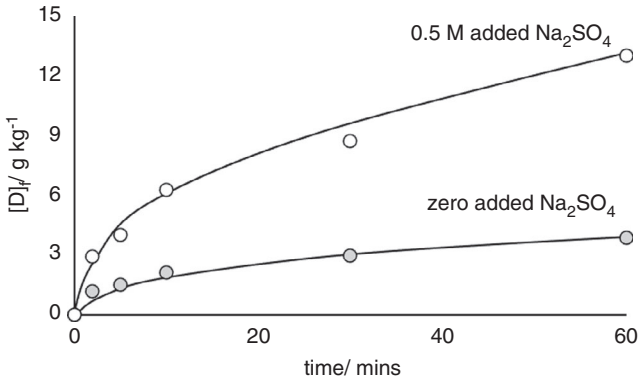

FIGURE 7 Effect of added Na_2SO_4 on the rate of uptake of purified C.I. Vat Green 1 on cotton; 50°C, 0.1 M NaOH; drawn using data from[64]

A large number of mathematical models have been developed to interpret the rate of diffusion of dyes within aqueous dyebaths and substrates of various structure and composition, which, traditionally, represent some or other interpretation of *Fick's 1st* or *2nd Laws of Diffusion*. Generically, as these *solutions* to Fick's 1st or 2nd Laws of Diffusion are mathematically very demanding and typically employ highly specific boundary conditions (e.g. infinite dyebath, circular cross section, short dyeing times, etc.), various *approximate solutions* have been devised which permit simplifying assumptions to be made regarding the calculation of values of *D*, using experimentally observed adsorption data, as illustrated by the widely used *Hill's equation*,[65] Equation 2, which is appropriate for the early stages of dyeing, where *r* is the radius of the (assumed) cylindrical substrate under consideration.

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{Dt}{\pi r^2}} \tag{2}$$

Studies of the diffusion of direct dyes within cellulosic fibres revealed the marked dependency of dye diffusion coefficient as a function of both dye concentration and amount of inorganic electrolyte,[39,40,56] as illustrated by the results presented in Figure 8, the reduction in diffusion coefficient observed at high amounts of added NaCl being indicative of dye aggregation.[33,40,57]

In the 1930s, it was proposed that the diffusion of direct dyes within cellulosic fibres could be described by the *porous matrix model* of dye diffusion,[19,22,33,68-70] according to which the dye molecules diffuse through a network of interconnected, water-filled *pores* in the cellulose polymer. When a diffusing dye collides with a *binding site* located on a pore wall surface, it can become adsorbed, or it can desorb from the collision site, re-enter the aqueous dye solution in the pores and diffuse further within the substrate. Although the pore model of dye diffusion has been applied to that of both reactive dyes (in the *absence* of dye-fibre reaction 22) and leuco vat anions, alternative models have also been proposed to account for the diffusional nature of various types of anionic dye in cellulosic fibres.[19,38,62,71-79]

Unfortunately, no single diffusional model has yet been devised that is able to satisfactorily account for the promotional effects of added NaCl or Na_2SO_4 on the uptake of dye anions on cellulosic fibres. This can be attributed in the most part, to the complex, intrinsically heterogeneous morphology and fine structure of cellulosic fibres, coupled with the complexities of water-inorganic electrolyte-dye anion interactions, etc. For example, the diffusion of reactive dyes in cellulosic fibres is a *heterogeneous process* insofar as the essentially mechanical *physisorption* of dye anions onto an appropriate adsorption site located on pore walls can be accompanied by the simultaneous *chemisorption* of the reactive dye anion onto an ionised hydroxyl group, Cell-O^-.[59,60,80-84]

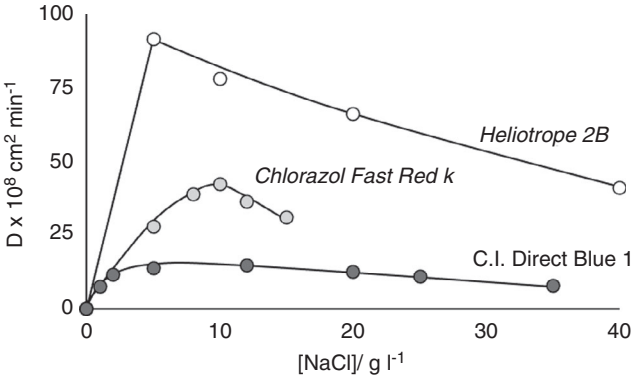

FIGURE 8 Effect of NaCl on the diffusion coefficient of C.I. Direct Blue 1 (101°C), *Heliotrope 2B* (100°C) and *Chlorazol Fast Red K* (90°C) in CV sheet; 0.05 g l^{-1} dye; drawn using data from[39,66,67]

However, in view of the limited, idealised and simplifying experimental conditions that are often typically employed in kinetic analyses of dyeing processes, which, for the most part, are unrepresentative of those encountered in real dyeing processes, it seems reasonable to once again pose the fundamental question as to exactly what type of information does the kinetic analysis of dye adsorption provide that is of relevance to the role of inorganic electrolytes in cellulosic fibre dyeing? The answer to this simple question is the same as that given above in the case of the thermodynamic analysis of aqueous dye adsorption processes, namely, *not very much actually*.

In order to consider the diverse assortment of theories/hypotheses/concepts which have been proposed to explain the promotional effect of added inorganic electrolyte on both the rate and extent of uptake of vat dyes, sulphur dye, azoic colorants, direct dyes and reactive dyes on cotton and other types of cellulosic fibre, involves discussions of the large and important fields of *electrolyte-water*, *electrolyte-fibre* and *electrolyte-dye* interactions, as viewed from the perspective of inorganic electrolytes; these particular facets of exhaust dyeing processes are discussed below.

In this context, although *qualitative research methods* characteristically utilise non-numerical data (e.g. video/in person interviews, market research, etc.) and which are widely employed in fields such as social sciences, education, health science, market research, etc., seek to understand a particular *phenomenon* by examining the totality of the underlying reasons/causes responsible for that phenomenon, in section 7 of this part of the paper, an essentially *phenomenological approach* to understanding the role of inorganic electrolyte in cellulosic fibres dyeing is presented. By examining the various hypotheses/theories, etc., which have been proposed to account for the role of salt in dyeing, in totality, an explanation has been identified which enables a mechanistic model to be constructed that accounts for the phenomenon both conceptually and practically, without recourse to the need to undertake complicated mathematical interpretation of experimentally observed dye adsorption data.

4 | ELECTROLYTE - WATER INTERACTIONS

The effects of electrolytes on the structure and properties of liquid water, from the perspectives of the influence of dissociated electrolyte anions and cations (e.g. Na^+, Cl^-, $SO_{4^{2-}}$, etc.) on the *solvation* of both ionised and neutral solutes by water, as well as the formation of *aqueous solutions* and *aqueous dispersions*, has received sizeable interest over a very long period of time. As the interactions of electrolyte anions and cations with water are of major significance in several areas of science and technology (e.g. biological processes, food technology, surface coatings, etc.), electrolyte-water interactions have been interpreted from various perspectives, including *water structure modification* (structure makers/structure breakers), *destabilisation of proteins* (kosmotropes and chaotropes), *precipitation of proteins* (Hofmeister series) and *protein solubility* (salting in/salting out) [e.g. [85-99]; for an introduction see [22] and the references therein]. Unfortunately, despite this attention, our knowledge and understanding of many aspects of the perplexing and complicated topic of electrolyte-water interactions are still not fully resolved.

Such is the magnitude and intricacy of these areas of study that only a necessarily very brief and superficial introductory account is presented here.

In essence, all types of ion interact with liquid water insofar as their electric fields disrupt the extensive, three-dimensional, H-bonded, dipolar water structure, to an extent that generally increases as a function of increasing ion size and charge (valency). Famously,[100] on the basis of the nature of their influence on water structure, ions can be viewed as being either *structure-makers* (i.e. promote water structure) or *structure-breakers* (i.e. diminish water structure): generally, smaller ions, such as Na^+, Ca^{2+} and Mg^{2+}, promote ordering of water molecules (i.e. promote water structure) and result in solutions that comprise a larger number of H-bonds and therefore display higher viscosity, than that of pure water, whereas large monovalent ions (e.g. Cl^-, NO_3^-, etc.) disorder water molecules and provide solutions of lower viscosity than pure water. The water structure-making/structure-breaking proficiencies of ions has been used to interpret the ability of *kosmotropic solutes* (small size, high charge density ions such as $SO_{4^{2-}}$ and Mg^{2+}) and *chaotropic solutes* (large size, low charge density monovalent ions such as NO_{3^-} and NH_4^+)[101] to stabilise or destabilise, respectively, proteins. In a related manner, according to the *Hofmeister Series*,[102,103] anions and cations can be classified according to their ability to either precipitate (*salt-out*) proteins, as exemplified by

Cl^- and $SO_{4^{2-}}$, or promote the dissolution of (i.e. *salt-in*) proteins, as illustrated by Na^+ and Ca^{2+} ions.

In effect, whilst the different classification systems referred to above seek to differentiate inorganic electrolyte anions and cations in terms of their ability to impart some or other effect upon the structure of water and/or the stability of proteins, the various systems display at least some level of commonality insofar as, the effects imparted by a given ion generally vary as a function of ionic size and ionic charge. Because of the effects which inorganic electrolyte ions exert upon the structure of water, it follows that these structural modifications will influence the interactions that occur between water and polar solutes (as well as non-polar solutes), which, from the viewpoint of this review, relates to dye/dye precursor anions.

5 | ELECTROLYTE - FIBRE INTERACTIONS

As mentioned, of the various theories/hypotheses/concepts which have been proposed to explain the remarkable promotional effect imparted by added inorganic electrolyte to both the rate (Figures 6 and 7) and extent (Figures 1 and 4) of anionic dye/dye precursor uptake on cellulosic fibres, the most commonly quoted postulate is that NaCl or Na_2SO_4 provides Na^+ cations which *neutralise* the negative charge that is developed at the surface of the fibre when it is immersed in water. Although this section of the review focusses primarily on this *fibre surface negative charge neutralisation* theory owing to its remarkable popularity, other, less commonly cited theories which invoke electrolyte-fibre interactions are also discussed.

5.1 | Fibre surface negative charge neutralisation

According to this theory, electrolyte-derived Na^+ cations suppress electrical repulsion forces operating between the negatively charged cellulosic fibre surface and the phenolate anions, Ar-O^-, in the case of azoic coupling components, enolate, -C-O^-, and thiolate, -S^-, anions, respectively, in the cases of vat dyes and sulphur dyes, as well as sulfonate anions, -$SO_{3^{2-}}$, in the cases of both direct and reactive dyes, in the aqueous dyebath. This expedites the operation of various types of intermolecular interaction, such as H-bonding, van der Waals forces, etc, between the dye and fibre, resulting in enhanced dye-fibre substantivity, which leads to increased dye uptake.

As such, this most popular of hypotheses of the role of added NaCl or Na_2SO_4 in cellulosic fibre dyeing correlates seamlessly with the various thermodynamic and kinetic theories, discussed in section 3, that have been proposed to explain the mechanism of direct dye adsorption on cellulosic

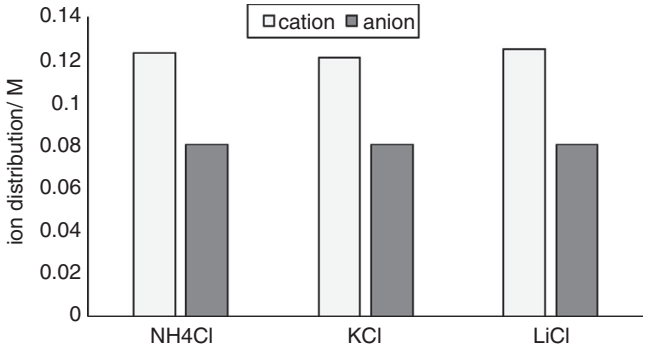

FIGURE 9 Distribution of inorganic electrolyte cations and anions between cellophane and aqueous 0.01 M inorganic electrolyte solution at 25°C; drawn using data from[12]

fibres and, by inference, the role of added inorganic electrolyte on dye uptake. Indeed, as discussed, these theories of dye adsorption are based on the fundamental assumption that a negative charge is developed at the cellulosic fibre-water interface and that this negative charge is increased by the presence of adsorbed dye/dye precursor anions.

A fundamental presumption of this *neutralisation theory* is that added inorganic electrolyte must be adsorbed by the cellulosic fibre during dyeing. This postulate was indeed confirmed experimentally insofar as an investigation into the role of added inorganic electrolyte in cellulosic fibre dyeing[12] revealed that both CV sheet and cotton adsorbed inorganic electrolyte-derived cations and anions from aqueous solution, though the distribution of the two types of ion between the cellulosic substrates and aqueous solution were disappointingly similar for different types of inorganic electrolyte (Figure 9). Intriguingly, of the various types of alkali metal electrolyte investigated, that most popularly utilised in cellulosic fibre dyeing, namely NaCl, was not included in this particular study.[12]

Unfortunately, the widely held hypothesis that the promotional effect of added inorganic electrolyte on anionic dye uptake is solely due to adsorbed Na^+ cations neutralising the negative charge developed at the fibre surface, is not only overly-simplistic but, more importantly, essentially flawed.[22,44] Nonetheless, the notion that added electrolyte suppresses electrical repulsion effects operating between the fibre surface and anionic dye/dye precursor anions merits consideration and discussion, simply because of its widespread popularity.

5.1.1 | The nature of the negative surface charge in cellulosic fibres

By way of background, all types of common textile fibre develop a negative charge when immersed in water[22,104-106] that arises from ionisation/dissociation of surface groups. As

discussed in the first part of the paper[1] the cellulose macromolecules in natural, regenerated and reconstituted cellulosic fibres contain two types of ionisable group that can give rise to the negative charge observed for cellulosic fibre surfaces in contact with aqueous solutions, namely carboxyl and hydroxyl.

Although -OH groups predominate, cellulosic fibres also comprise relatively small amounts of -COOH groups which arise due to partial oxidation processes encountered during fibre production, notably bleaching [see 22 and the references therein]. Values reported for the carboxyl and hydroxyl content of cellulosic fibres and other types of cellulosic materials vary depending on the nature of the substrate and the method of determination employed [e.g. -COOH content of cotton: 0.002-0.005 mol kg^{-1},[107] 0.006 mol l^{-1};[108] -OH content of cotton 10.15-11.22 mol l^{-1}[109]].

Zeta potential, which is a measurable attribute of the *electrical double-layer* established at the surface of a charged substrate, such as that of a textile fibre, when immersed within a polar liquid such as water,[22,104,105,110,111] is widely used to quantify the surface charge developed at fibre (and polymer) surfaces under aqueous conditions.

By way of brief explanation, owing to the charge that is developed at a textile fibre surface under aqueous conditions, such as those within a solution that comprise dissociated ions, such as a typical aqueous dyebath, an *electric double-layer* is developed at the surface which consists of an *inner lay*er that contains a predominance of *counterions* (ions of opposite charge to that of the surface) and an *outer layer* or *diffuse layer* that contains both counterions and *coions*. The charged surface therefore influences the ionic environment (i.e. the counterion/coion concentration distribution) of the aqueous solution that is in close proximity to the surface. This results in the development of an *electrical potential*, ψ, within the electric double layer that decreases, exponentially, from its maximum value at the charged surface to zero within the bulk aqueous solution. The presence of an electric double-layer at solid/liquid interfaces results in several *electrokinetic phenomena*, such as *streaming potential*, *electro-osmosis*, *electrophoresis*, *sedimentation potential* and, of relevance to this discussion, *zeta potential*, *ζ-potential*.[112-115]

The zeta-potential of a given type of fibre surface depends on several factors related to both the substrate (e.g. surface structure, porosity, nature of the underlying polymer, etc.) and the aqueous background electrolyte solution (e.g. KCl) utilised in the *electro-osmosis* method that is employed to determine ζ-potential. Briefly, values of zeta-potential are negative for all types of fibre in distilled water (e.g. ζ-potential/mV: cotton −28; PA 66 −37; PET −52 Ref. 116) and become increasingly more negative with increasing pH; similar pH-dependent zeta-potential profiles are observed for various types of natural, man-made and synthetic fibre.

In the case of cotton immersed in water, ζ-potential decreases exponentially (i.e. becomes more negative) over the pH range 2 to 9,[104,105,117,118] owing to the presence of ionised carboxyl groups (Cell-COO^-), with a plateau region occurring at pH values of ~6-9 due to complete dissociation of the weakly acidic -COOH groups (e.g. pK_a of -COOH groups in cotton 2.95 Ref. 119).

From the viewpoint of this review, the presence of relatively very small amounts of -COOH groups within cellulose macromolecules is of significance because of two observed phenomena that are each a consequence of the intrinsic weakly acidic nature of the carboxylic acid group. Firstly, owing to their low pK_a values, the carboxyl groups readily dissociate under aqueous conditions, furnishing ionised -COO^- groups that reside within the cellulosic fibre and which are the major contributor to the observed negative charge developed at cellulosic fibre surfaces in aqueous solution. Secondly, it has been demonstrated that the uptake of anionic dyes onto cellulosic fibres decreases as the carboxyl group content of the substrate increases, this being attributed to increasing Cell-COO^- group-derived negative surface charge.[3,108,120,121]

The zeta potential for cotton gradually becomes more negative at pH values > 10[122-124] because of the presence of ionised hydroxyl groups, Cell-O^-. However, because the -OH groups in cellulose behave as very weak acids, as evidenced by the widely quoted value of $K_a = 1.84 \times 10^{-14}$ at 25°C recorded by Neale[125] which corresponds to a pK_a of 13.73, so the degree of dissociation of the hydroxyl groups will be very low <pH ~ 13.73 [e.g. dissociation/%: 0.1 @ pH 10.73; 1 @ pH 11.73; 10 @ pH 12.73; 50 @ pH 13.73 [22]]. Such markedly pH-dependent dissociation behaviour means that the contribution which ionised -OH groups make towards measured zeta potentials of cotton (and other types of cellulosic fibre) will only be of consequence at higher pH values (i.e. ~>pH 10). As this latter characteristic attribute of the component hydroxyl groups in the cellulose polymer is of relevance in terms of the electrolyte-induced *surface charge neutralisation theory*, it is discussed in section 5.2.

Furthermore, the contribution that -OH groups make towards the zeta-potential observed for natural, regenerated and reconstituted cellulosic fibres will be further compromised because[1] the primary (C-6) and two secondary (C-2 and C-3) -OH groups in the constituent cellulose macromolecule display markedly different reactivity owing to their respective alcoholic behaviour, as well as their involvement in intramolecular/intermolecular H-bonding and location within elementary fibril surfaces.[126-130] As such, the principal contributor to the negative zeta potential recorded for cellulosic fibre surfaces in aqueous solution and, by extension, to the negative charge developed at the cellulosic substrate surface, seems likely to arise primarily from dissociation of the -COOH groups; this is further discussed in section 5.2.

Unfortunately, the theory that inorganic electrolyte increases the uptake of anionic dyes/dye precursors on cellulosic fibres by neutralising negative surface charge gains little support from evidence provided by studies of the ζ-potential of such fibres, as well as that of other related electrokinetic parameters, such as specific charge, *q*, isoelectric point (*IEP*) and point of zero charge (*PZC*) [see 22 and the references therein].

For example, values of zeta potential measured for different types of cellulosic fibre do not correlate with -COOH group content, even though carboxyl group content correlates with observed reduction of anionic dye uptake.[22] Moreover, although added NaCl has been shown to reduce the negative ζ-potential of cotton,[106] analysis of the experimental data [22] reveals that the amount of Na^+ cations required to 'neutralise' the negative charge developed at the cotton fibre surface derived from the presence of Cell-COO^- and Cell-O^- groups accounted for only a small proportion of the added inorganic electrolyte that is typically utilised in cotton dyeing, especially in the case of the application of reactive dyes. In view of the relevance of the latter phenomenon to the popular surface charge neutralisation theory, this is discussed below.

5.1.2 | Amount of inorganic required to 'neutralise' the negative surface charge

According to the notion that added electrolyte 'neutralises' the negative charge developed at the surface of cellulosic fibres in aqueous solution, an approximate idea of the likely amount of added NaCl or Na_2SO_4 that would theoretically be required to overcome the negative charge derived from ionised carboxyl groups, Cell-COO^-, and their ionised hydroxyl group, Cell-O^-, counterparts, in a cellulosic substrate, can be inferred from knowledge of the relative amounts of these two types of polar group present within the substrate and their dissociation behaviour.[22]

For the purposes of this brief discussion, the most popular of all cellulosic fibres, cotton, will be selected for consideration. If it is assumed that cotton contains 0.005 mol kg^{-1}[107] of accessible, ionised -COOH groups, the amount of, for example, NaCl required to 'neutralise' all of the Cell-COO^- groups in the component cellulose macromolecule can be estimated, presuming, very simply, that an equivalent amount of Na^+ cations is provided in the form of NaCl. Accordingly, 0.005 mol or 0.292 g [NaCl = 58.4 g mol^{-1}], of NaCl per kg of fibre would be required to 'neutralise' the 0.005 mol kg^{-1} of Cell-COO^- groups in the substrate, which equates to 0.0292 g kg^{-1} in the case of exhaust dyeing using a 1:10 liquor ratio (the basis of the latter calculation is explained below in the case of the -OH groups in cotton).

Although the theoretical maximum amount of -OH groups in cellulose is ~18.5 mol kg^{-1},[131,132] only the relatively small proportion of this maximum number of hydroxyl groups which are located within non-crystalline regions will be accessible to interactions with water and dissolved species, such as dye molecules. As values recorded for the crystallinity of cotton vary, over a wide range, depending on the type of cotton and the method of determination employed [e.g. crystallinity/%: 39-95%,[133] 74-78.5,[134] 85,[135] 91[136]], the fraction of amorphous material present within cotton may well be of the order of ~30%, though a value as low as 5-14% has been suggested.[132] Briefly, assuming that cotton is ~70% crystalline means that of the theoretical maximum ~18.5 mol kg^{-1} [131,132] of -OH groups in cellulose, some ~5.52 mol kg^{-1} will be available within the remaining 30% amorphous regions. This means that 5.52 mol or ~322.4 g of NaCl per kg of cotton would be required in order to achieve 'neutralisation' of the Cell-O^- groups, which corresponds to 32.2 g kg^{-1} in the case of dyeing using a 1:10 liquor ratio; the effect of dyebath volume (i.e. liquor ratio) on the dyebath concentration of added electrolyte is discussed below.

However, because of their marked pH-dependent dissociation behaviour, the amount of ionised -OH groups present within the non-crystalline regions of cotton will depend upon the particular pH of interest [e.g. -OH group dissociation/%[22] (available Cell-O^- groups in cotton/mol kg^{-1}): 0.1 (0.0055) @ pH 10.73; 1 (0.055) @ pH 11.73; 10 (0.55) @ pH 12.73, assuming -OH group content of amorphous domains = ~5.52 mol kg^{-1} and pK_a of -OH groups = 13.73]. Because of this pronounced pH-dependent variation in the number of ionised hydroxyl groups present within the non-crystalline regions of cotton, so the amount of NaCl required to compensate for the Cell-O^- groups will also be pH-dependent [e.g. -OH group dissociation/%[22] (amount of NaCl required to 'neutralise' available Cell-O^- groups/g kg^{-1}): 0.1 (0.32) @ pH 10.73; 1 (3.22) @ pH 11.73; 10 (32.2) @ pH 12.73, assuming OH group content of amorphous domains = ~5.52 mol kg^{-1} and pK_a of -OH groups = 13.73 [125]].

Moreover, owing to the previously discussed differing reactivity, relative involvement in intramolecular/intermolecular H-bonding and location within elementary fibril surfaces, of the three types of -OH group in the constituent cellulose polymer molecule, the value of ~5.52 mol kg^{-1} of available -Cell-O^- groups present within the non-crystalline regions, and therefore the amount of NaCl required to achieve 'neutralisation', may well be unrealistically high. Indeed, in the case of bulky dye molecules, such as reactive dyes, it has been suggested that the accessible regions correspond to between just 0.029 and 0.24 mol kg^{-1}.[132]

According to these rudimentary assumptions, a simple, unsophisticated but nonetheless instructive estimate of the amount of added inorganic electrolyte that would theoretically be required to 'neutralise' or compensate for, the negative surface charge developed in 1 kg of cotton due to the

TABLE 1 estimate of the amount of NaCl required to 'neutralise' Cell-O^- and Cell-COO^- groups in 1 kg of cotton, assuming pH-dependent maximum of 5.52 mol kg^{-1} of Cell-O^- groups, corresponding to 322.4 g of NaCl per kg of cotton fibre and pK_a of 13.73 for the Cell-OH groups, as well as 0.005 mol kg^{-1} of available Cell-COO^- groups, corresponding to 0.292 g of NaCl per kg of cotton fibre and pK_a of 2.95 for the Cell-COOH groups

Dye class	pH range typically used in immersion dyeing[1]	pH-dependent degree of dissociation of -OH groups/%[22]	pH-dependent amount of NaCl required to 'neutralise' Cell-O^- groups/g kg^{-1} of fibre	Total pH-dependent amount of NaCl required to 'neutralise' both Cell-O^- and Cell-COO^- groups in fibre/g kg^{-1}	Typical range of NaCl used in immersion dyeing/g l^{-1}[11]	Typical dyebath concentration of NaCl required for immersion dyeing @ 1:10 LR/g l^{-1}	Dyebath concentration of NaCl required to 'neutralise' both Cell-COO^- and Cell-O^- groups in fibre @ 1:10 LR/g l^{-1}
Vat	12-13	1-10	3.22-32.2	3.5-32.5	5-40	50-400	0.35-3.25
Sulphur	10-11	0.1	0.32	0.35	5-20	50-200	0.035
Azoic colorant	12-13	1-10	3.22-32.2	3.5-32.5	10-40	100-400	0.35-3.25
Direct	6-7	0	0	0.292	5-15	50-150	0.029
Reactive	10-12	0.1-1	0.32-3.22	0.35-3.5	30-100	300-1000	0.035-0.35

presence of both Cell-COO^- and Cell-O^- groups, can be undertaken.

A range of pH values and amounts of added inorganic electrolyte are typically utilised for the exhaust application of each of the five classes of anionic dye/dye precursor to cellulosic fibres,[1,22,137-139] as illustrated by the data shown in Table 1 for cotton.

Of the five classes of dye listed in Table 1, this discussion will be initially confined to that of the most popular of types of dye employed for cellulosic fibres, namely reactive dyes. Under the typical alkaline application conditions utilised to apply reactive dyes to cotton (i.e. ~pH 10 to 12; Table 1), because the 0.005 mol kg^{-1} of carboxyl groups in the fibre will be fully ionised (i.e. pK_a of 2.95 [119]) then 0.292 g of NaCl would be required to 'neutralise' the resulting Cello-COO^- groups within the substrate. Owing to the marked pH-dependency of the ionisation of the 5.52 mol kg^{-1} of hydroxyl groups in cotton, the degree of dissociation will range between ~0.1% (at pH 10.73) and 1% (at pH 11.73) (Table 1), so that the corresponding amount of NaCl required to 'neutralise' the resulting Cell-O^- groups within the fibre will correspond to between 0.32 and 3.22 g kg^{-1} (column 4 in Table 1).

Column 5 in Table 1 shows that a total of between 0.35 and 3.25 g of NaCl would therefore be theoretically required to 'neutralise' the surface negative charge of the cotton fibre derived from the Cell-COO^- and pH-dependent Cell-O^- groups available over the pH range of 10 to 12. As this amount of added NaCl depends on the mass of fibre used, it is a *fibre-dependent variable*, expressed as g of NaCl per kg of cotton fibre, and is a function of both the pH utilised for dyeing and the respective degree of dissociation of the available -COOH and -OH groups in the substrate.

The amount of added inorganic electrolyte that is typically required to be added to an immersion dyebath in order to promote uptake of each of the five classes of anionic dye/dye precursor to cellulosic fibres (column 6 in Table 1) is a *dyebath-dependent variable* insofar as the amount of added NaCl (or Na_2SO_4) employed is expressed in terms of the volume of the dyebath liquor via the dyebath parameter, *liquor ratio* (LR). Because dyebath volume increases with increasing LR, so the amount of added NaCl increases correspondingly, since a desired level of inorganic electrolyte concentration in the aqueous dyebath is required; as such, the amount of added inorganic electrolyte required for dyeing is expressed in dyebath-dependent units, commonly g l^{-1} (column 6 in Table 1).

If it is assumed for the purposes of this discussion, that a 1:10 liquor ratio was used to apply the reactive dye to cotton, the dyebath volume-dependent amounts of NaCl required for dyeing, namely 30 to 100 g l^{-1} (column 6 in Table 1), will be *amplified* by a factor of 10 because of the presence of 10 L of dyebath liquor imposed by the assumed 1:10 LR and the

requirement to achieve a desired level of inorganic electrolyte concentration in the aqueous dyebath. In this case, the corresponding *dyebath concentration* of NaCl will be in the range of 300 to 1000 g l^{-1} (column 7 in Table 1).

In contrast, when the fibre-dependent amounts of NaCl required to 'neutralise' the Cell-COO^- and Cell-O^- groups in the cotton fibre, namely 0.35 to 3.25 g kg^{-1} (column 5 in Table 1) are expressed in dyebath-dependent units related to the dyebath volume employed for dyeing (i.e. *dyebath concentration*: unit g l^{-1}), using a 1:10 LR means that these fibre-dependent amounts of added NaCl will be *reduced* by a factor of 10, owing to the diluting effect imposed by the 10 L of dyebath liquor. As Table 1 reveals, in the case of a reactive dye, the dyebath concentration of NaCl required to 'neutralise' both the Cell-COO^- and Cell-O^- groups in the substrate will be in the range 0.035 to 0.35 g l^{-1}, in the case of a 1:10 LR (column 8 in Table 1).

The above very simple calculations reveal that although typically 300 to 1000 g l^{-1} of NaCl may be added to an exhaust dyebath when a reactive dye is applied to cotton at pH 10-12 using a 1:10 LR (column 7 in Table 1), the magnitude of these additions bears no correlation with the 0.035 to 0.35 g l^{-1} of NaCl that would theoretically be required to be present in the dyebath in order to 'neutralise' the negative surface charge derived from both the Cell-COO^- and Cell-O^- groups in the substrate (column 8 in Table 1).

These somewhat very rudimentary estimations, which are summarised in Table 1 for each of the five classes of anionic dyes/dye precursors of relevance to this review, suggest that the levels of inorganic electrolyte likely utilised in the immersion dyeing of cotton (and, by extension, to other types of cellulosic fibre) in order to promote dye uptake are considerably in excess of those required to 'neutralise' or compensate for the negative charge developed at the surface of the fibres under typical dyebath conditions, assuming complete ionisation of all Cell-COOH groups and the pH-dependent dissociation of available Cell-OH groups in the substrate. This situation is illustrated graphically in Figure 10 in the case of dyebaths of varying LR.

The left hand plot in Figure 10 shows that whilst the amount of added NaCl typically utilised in applying the five classes of dye to cotton increases with increasing LR, from 1:3 to 1:10, as shown by the solid shaded vertical bars, the fibre-dependent amount of NaCl required to 'neutralise' all of the Cell-COO^- and Cell-O^- groups in the cotton substrate, as shown by the dashed horizontal bars, is, of course, independent of the volume of the aqueous dyebath (i.e. independent of LR). The large differences between the amounts of added inorganic electrolyte required to neutralise the negative charge associated with the Cell-COO^- and Cell-O^- groups in the substrate (dashed horizontal bars) and the amounts of added electrolyte typically employed in exhaust dyeing (shaded vertical bars) is clearly evident; these aspects are discussed in the section below. The right hand plot in Figure 10 shows an expanded view of the dyebath volume-independent amounts of NaCl required to 'neutralise' both types of polar group in the fibre for the three different liquor ratios selected, over the range 0 to 50 g kg^{-1} NaCl.

From the above brief discussion, it seems reasonable to suggest that whilst the adsorption of inorganic electrolyte-derived Na^+ cations may well suppress electrical repulsion forces operating between the negatively charged cellulosic fibre surface and adsorbing dye/dye precursor anions, it seems unlikely that the promotional effect of added inorganic electrolyte on anionic dye/dye precursor uptake is attributable merely to adsorbed Na^+ cations neutralising the negative charge developed at the fibre surface for two main reasons. Firstly, only very small amounts of added Na^+ cations are required to overcome the negative charge associated with the Cell-COO^- and Cell-O^- groups in the substrate and, secondly, the amounts of added electrolyte typically employed in exhaust dyeing are several orders of magnitude greater than those required to 'neutralise' surface charge, as illustrated by the data presented in Table 1 and Figure 10.

The highly popular electrolyte-induced surface charge neutralisation theory can therefore be considered to provide an unsatisfactorily robust and unconvincing explanation of the mechanism by which added NaCl or Na_2SO_4 promotes anionic dye uptake; indeed, at very best, it offers only an incomplete, overly-simplistic description.[22,44]

5.1.3 | Amount of inorganic electrolyte employed in dyeing

The Na^+ cations that will be present within a typical aqueous dyebath encountered during cellulosic fibre dyeing will be derived from sources other than added NaCl or Na_2SO_4. These include commercial grade direct dyes and reactive dyes which are commonly supplied as the sodium salt (D-SO_3Na) rather than the corresponding free acid variant (D-SO_3H), as well as the various types of reductant, such as sodium dithionite, $Na_2S_2O_4$, and sodium sulfide, Na_2S, which are utilised in the application of vat dyes and sulphur dyes, respectively, together with different types of alkali, such as NaOH and Na_2CO_3, that are required for applying azoic coupling components, vat dyes and reactive dyes.

The discussion in section 5.2 regarding the likely amounts of Cell-COO^- groups present in cotton revealed that even in the absence of added inorganic electrolyte, the Na^+ cation content of typical dyebaths used for dyeing cellulosic fibres may well be sufficiently high enough to 'neutralise' the negative potential associated with the surface Cell-COO^- groups in the substrate. A similar argument might apply in the case of the Cell-O^- groups which can be present in cellulosic fibres such as cotton. Because ionisation of the -OH groups

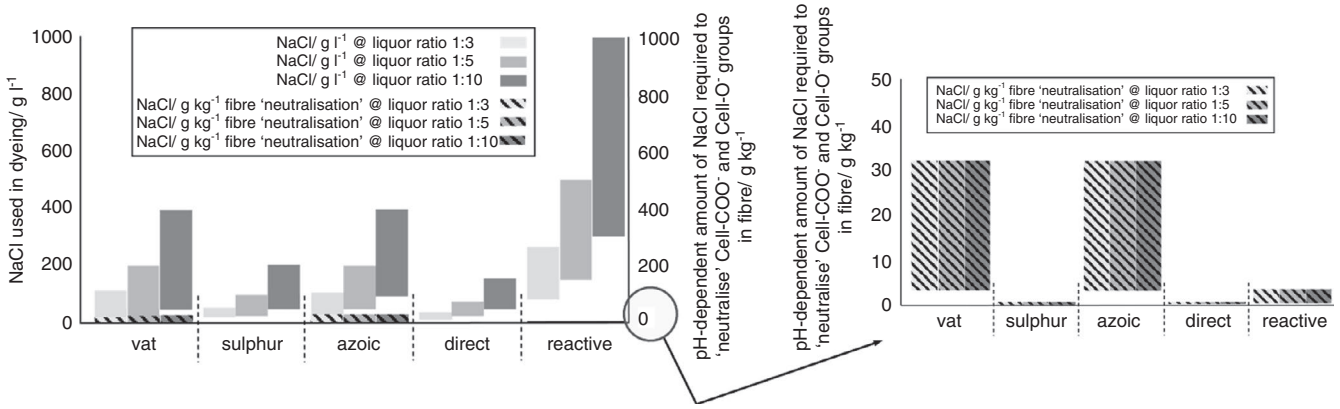

FIGURE 10 Effect of liquor ratio on NaCl dyebath usage assumed for each of the five classes of dye being applied to 1 kg of cotton superimposed on the amount of NaCl required to achieve 'neutralisation' of available Cell-COO^- and Cell-O^- groups in cotton; assumes 0.005 mol kg^{-1} of Cell-COO^- groups and maximum of 5.52 mol kg^{-1} of Cell-O^- groups, equivalent to 0.292 g kg^{-1} and ~322.4 g kg^{-1} NaCl, respectively; pK_a of -Cell-COOH groups = 2.95; pK_a of Cell-OH groups = 13.73; pH-dependent dissociation of Cell-OH groups estimated using the Henderson-Hasselbalch equation[22]

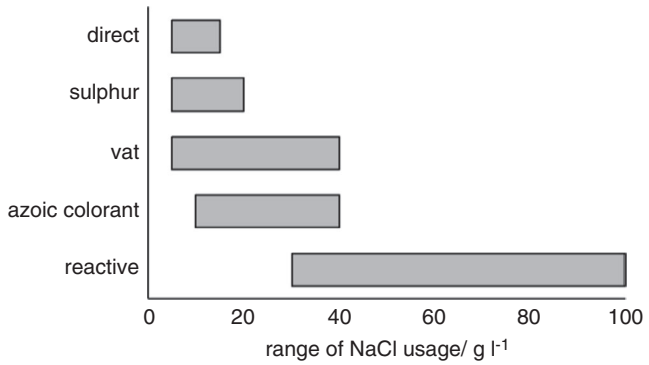

FIGURE 11 Typical amounts of NaCl required for immersion dyeing of cotton according to dye class; drawn using data from[1]

TABLE 2 variation of the amount of added NaCl/g l^{-1} required for the exhaust application of *Novacron FN* (Huntsman) dyes to cellulosic fibres in the presence of Na_2CO_3, as a function of liquor ratio and amount of dye applied[142]

	Dye applied/% omf						
Liquor ratio	**<0.5**	**0.5**	**1**	**2**	**3**	**4**	**≥5**
≤1:6	10	20	30	40	50	60	70
1:6 < LR ≤1:8	20	30	40	50	60	70	80
>1:8	30	40	50	60	80	90	100

is decidedly pH-dependent (Table 1) so it can be considered that whilst higher dyebath pH will result in greater amounts of anionic Cell-O^- groups, such alkaline dyebaths will also contain correspondingly higher amounts of auxiliary chemicals, such as NaOH, Na_2SO_4, NaCl, Na_2CO_3, Na_2S, etc., depending on the class of dye involved, that will, in turn, furnish higher levels of sodium cations.

Nonetheless, as Figure 10 reveals, there is a considerable difference between the quantity of NaCl required to overcome the negative surface charge associated with both the Cell-O^- and Cell-COO^- groups in cotton and the amounts of NaCl utilised in typical immersion dyeing processes. The fact that substantial amounts of additional Na^+ cations are required to be added to the dyebath in the guise of NaCl or Na_2SO_4, so as to further 'neutralise' the negative fibre surface potential, seems to be not only excessive but somewhat far-fetched.

For example, as discussed in section 5.2 and the first part of the paper,[1] each of the five types of anionic dye/dye precursor typically require different amounts of added inorganic electrolyte for their application to cotton, which follows the approximate order direct dyes < sulphur dyes < azoic coupling components < vat dyes <<< reactive dyes, this being conveniently illustrated by Figure 11.

If added inorganic electrolyte were to promote dye/dye precursor anion uptake solely by the added Na^+ cations neutralising the negative charge at the fibre surface, it follows that exactly the same amount of electrolyte would be required for the application of each of the five types of dye/dye precursor anions to the same sample of cotton, which clearly is not the case (Figure 11). This is highlighted by the fact that for the same cotton substrate, Figure 11 reveals that the amount of added NaCl required to apply reactive dyes is several times greater than that required for each of the other classes of anionic dye/dye precursor.

Furthermore, as previously recounted,[1] the amount of inorganic electrolyte added to reactive dye dyebaths varies according to the liquor ratio selected for dyeing, as illustrated by the data presented in Table 2, which, it must be emphasised, are representative of the crucially important and critically helpful type of information provided by the makers of commercial ranges of reactive dyes. In this context, because the amounts of electrolyte required for exhaust dyeing will vary as a function of both LR and amount of dye applied for

different commercial ranges of reactive dyes,[140-144] the data presented in Table 2 were chosen arbitrarily as being representative of information provided by dye makers.

This particular facet of reactive dye application further controverts the notion that added Na^+ cations neutralise the negative charge developed at the cellulosic fibre surface. Changing the liquor ratio used for dyeing *only* changes the volume of the aqueous dyebath. It does not in any way change the nature or magnitude of fibre surface charge nor the anionicity of the reactive dyes in the dyebath, since the latter characteristic attribute of common reactive dyes is invariably provided by sulfonate groups, $-SO_3Na$, which possess pK_a values of $\sim<1$, which means that the dyes are fully ionised (and thus complete anionicity is achieved) at pH values $\sim\geq1$.

In addition, as discussed,[1] the amount of inorganic electrolyte added to reactive dye dyebaths also varies according to the amount of reactive dye applied. Once again, this particular characteristic of reactive dye application fails to support the concept that added Na^+ cations neutralise the negative charge developed at the fibre surface. Changing the amount of dye applied to cotton or other type of cellulosic fibre clearly cannot modify either the nature or magnitude of the fibre surface charge - it *only* changes the quantity of anionic reactive dye present in the dyebath.

In the latter context, Table 2 shows that as the amount of *Novacron FN* (Huntsman) reactive dye applied to cellulosic fibres increases so does the amount of added NaCl required for dyeing. Such increases in the quantity of added NaCl that accompany an increase in the amount of dye applied may be necessary to compensate for the corresponding increase in the anionicity of the aqueous dyebath phase that accompanies an increase in the amount of anionic dye present in the dyebath. Such a proposal appears reasonable, based on the fact that as the amount of reactive dye applied to the substrate increases, so the quantity of ionised (i.e. anionic) reactive dye present in the dyebath increases, which, it can be considered, may well result in greater electrical repulsive forces operating between the negatively charged, fully dissociated sulfonate anions, $D\text{-}SO_{3^-}$, in the dye molecules and the negatively charged cellulosic fibre surface.

If this were the case, it follows that a simple relationship should exist between the amount of reactive dye applied to the substrate, which can be considered to provide an approximate measure of the anionicity of the dyebath as derived from the $D\text{-}SO_{3^-}$ anions present, and the amount of added NaCl required for dyeing, which can be considered to provide an approximate measure of the Na^+ ion content of the dyebath.

Using the data presented in Table 2 such a relationship is indeed observed (Figure 12) in the case of a liquor ratio of 1:6, although some deviation from linearity is secured for a liquor ratio of 1:10.

However, as discussed in section 5.2, because the amount of dye used in exhaust dyeing is a fibre-dependent variable,

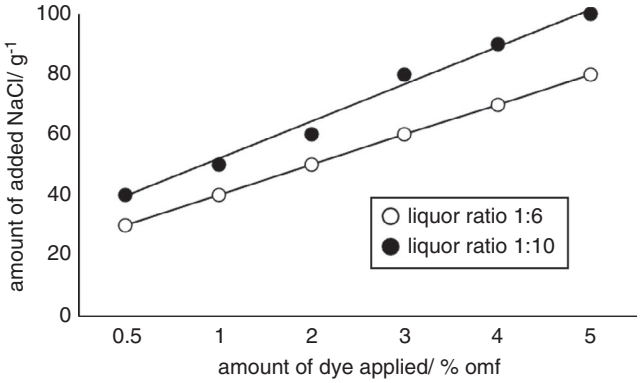

FIGURE 12 Relationship between the amount of added NaCl required for dyeing 1 kg of cellulosic fibre and the amount of *Novacron FN* (Huntsman) dye applied for liquor ratios of 1:6 and 1:10; drawn using data from Table 2[140]

the concentration of dye in an aqueous dyebath will vary according to liquor ratio (i.e. volume of the aqueous dyebath). This situation is illustrated by Figure 13 which shows how changes in dyebath volume that accompany a change in liquor ratio over the range 1:4 to 1:10, influence the concentration of dye in the ensuing dyebath, in the case of amounts of applied dye ranging from 0.5% omf to 5% omf; the figures shown on the graph denote the particular value of liquor ratio examined.

Figure 13 reveals that a non-linear relationship is secured for the variation of dyebath dye concentration as a function of dyebath volume (i.e. liquor ratio), for each of the five values of applied dye examined. When the NaCl usage data presented in Table 2 is interpreted in terms of the non-linear dependency of dyebath dye concentration on dyebath volume depicted in Figure 13, a distinctly non-linear relationship is also observed (Figure 14) between the concentration of added NaCl present in the dyebath and the concentration of reactive dye in the dyebath, for the application of different amounts of dye over the range 0.5% omf to 5% omf to 1 kg of cellulosic fibre, in the cases of liquor ratios of both 1:6 and 1:10.

Comparison of Figures 12 and 14 shows that the essentially linear plots observed for the variation in the amount of added NaCl required for applying the *Novacron FN* (Huntsman) dyes to cellulosic fibres as a function of the amount of dye applied over the range 0.5% omf to 5% omf at liquor ratios of 1:6 and 1:10 (Figure 12), which are reasonably similar in both shape and magnitude for the two liquor ratios examined, do not reflect the decidedly non-linear plots secured for the variation in the dyebath concentration of NaCl that occurs over the same particular range of dyebath dye concentration examined (Figure 14), which are much less similar in both shape and magnitude, especially in the case of the 1:10 liquor ratio. Indeed, as the arrowed lines in Figure 14 reveal, the concentration of added NaCl required for a given applied depth of shade, say 2% omf, at a liquor

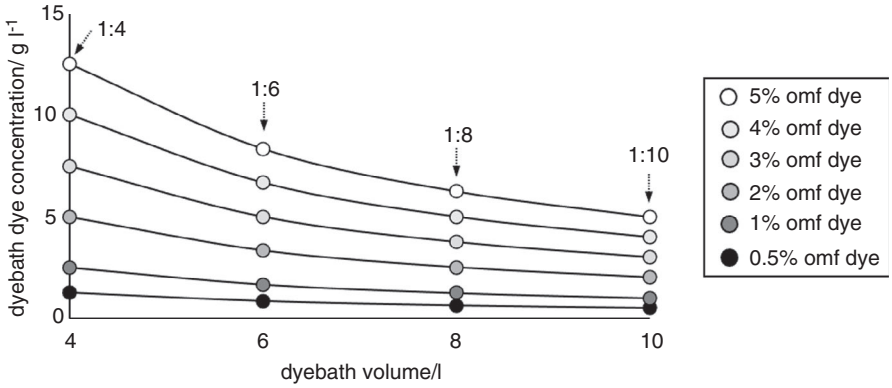

FIGURE 13 Variation of dyebath dye concentration as a function of dyebath volume, for the application of different amounts of dye over the range 0.5% omf to 5% omf to 1 kg of cotton over the liquor ratio range 1:4 to 1:10

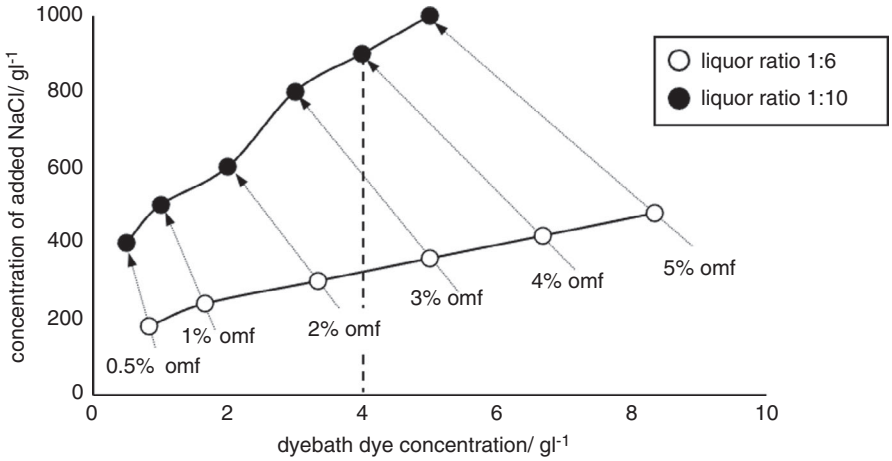

FIGURE 14 Relationship between the concentration of added NaCl in the dyebath and the dyebath concentration of *Novacron FN* (Huntsman) dyes applied to 1 kg of cellulosic fibre over the range 0.5% omf to 5% omf, for liquor ratios of 1:6 and 1:10; drawn using data from Table 2[141]

ratio of 1:6 must be increased, considerably, when a liquor ratio of 1:10 is employed.

Interestingly, Figure 14 also shows that the application of 5% omf dye employing a 1:10 liquor ratio necessitates the use of 1 kg of NaCl for each kg of fibre dyed; whilst this high level of electrolyte usage is reduced to ~0.5 kg of NaCl per kg of fibre dyed when a 1:6 liquor ratio is utilised, such routinely high levels of dyebath salinity of course pose potentially sizeable economic and environmental concerns.

It can therefore be concluded that the increase in the amount of added NaCl that accompanies an increase in the amount of dye applied to cellulosic fibres, as depicted by the data presented in Table 2, does not compensate for the corresponding increase in the (reactive dye) anionicity of the aqueous dyebath phase and the purportedly greater ensuing electrical repulsive forces operating between the negatively charged sulfonated dye anions and the negatively charged fibre surface. Indeed, as Figure 14 reveals, for a given concentration of dye in the dyebath, and therefore, for essentially a given level of dyebath dye anionicity, a considerably larger concentration of added NaCl is required for a 1:10 liquor ratio dyebath than a 1:6 liquor ratio dyebath, for example, as shown by the dashed line in Figure 14 in the case of 4 g l^{-1} dye. Thus, whilst adding more reactive dye to a dyebath will of course increase the concentration of dyebath dye anions, the reason for needing to increase the amount of inorganic electrolyte in the dyebath is not simply to offset the ensuing increased dyebath anionicity. As Figure 14 further shows, the relationship between the concentration of added inorganic electrolyte in the dyebath and the concentration of dye in the dyebath is far from straightforward, because of the complicating effect of liquor ratio (i.e. dyebath volume).

This latter proposal garners support from the plots presented in Figure 15 which highlight the fact that the essentially linear increase in the amount of added NaCl that accompanies an increase in the amount of dye applied to cellulosic fibres as described in Table 2 (represented by the solid lines in Figure 15), does not reflect the corresponding nonlinear increase in dyebath dye concentration that accompanies an increase in the amount of dye applied (as represented by the bars and dashed lines in Figure 15).

Moreover, the surface charge neutralisation theory, which seeks to ascribe the promotional effect of added inorganic electrolyte in cellulosic fibre dyeing solely to suppression of negative charge developed at the fibre surface, lacks credibility from a mechanistic viewpoint. For example, assuming that in order for the Na^+ ions to suppress negative surface charge, the primary role of the sodium cations which are derived from the added NaCl or Na_2SO_4, is to become adsorbed onto the Cell-COO^- groups and, depending on dyebath pH, Cell-O^- groups, that are situated along cellulose macromolecular chains within the amorphous domains in the

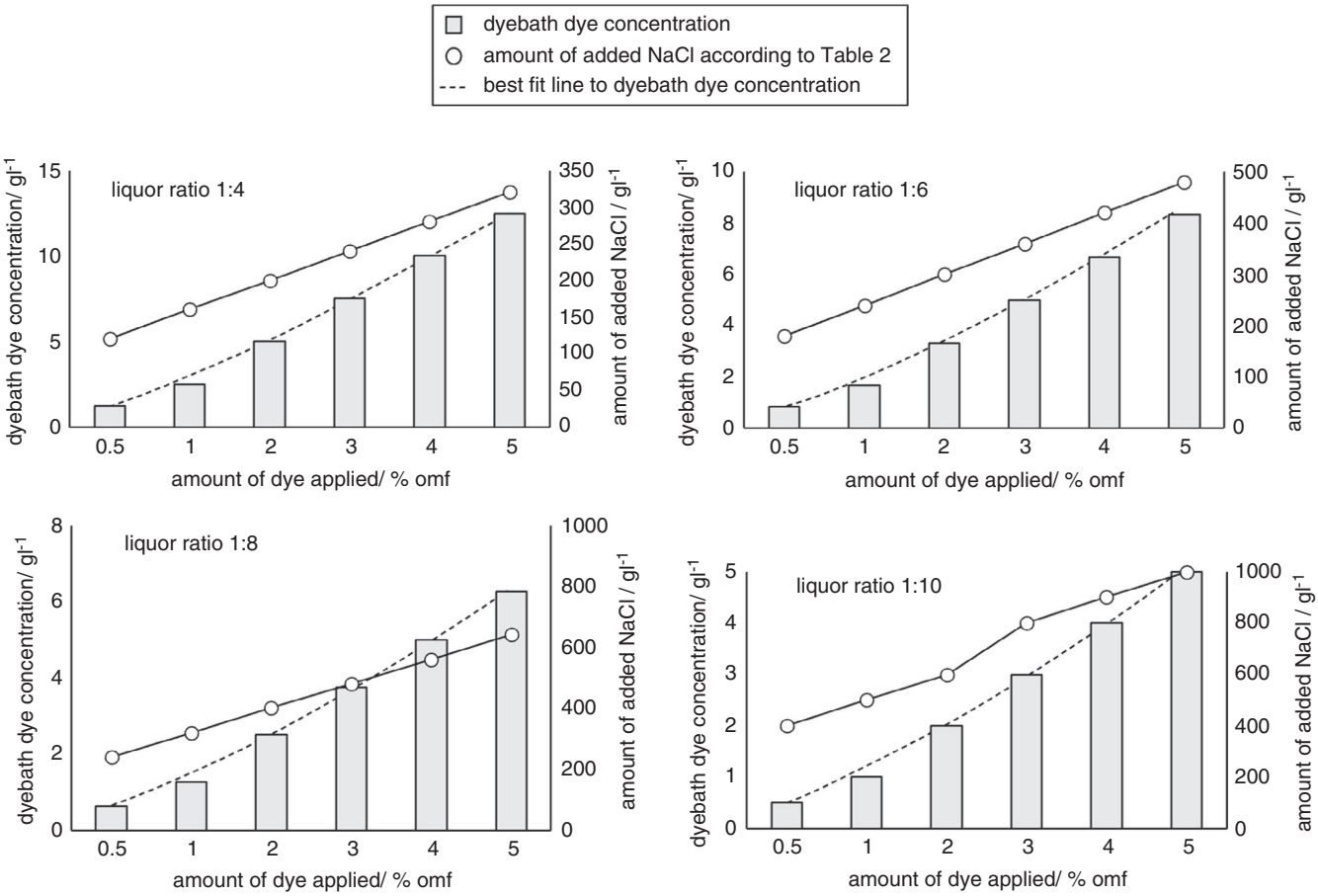

FIGURE 15 Variation of dyebath dye concentration and amount of NaCl required for applying *Novacron FN* (Huntsman) dyes to 1 kg of cellulosic fibre as a function of the amount of dye applied; drawn using data from Table 2 [61]

cellulosic fibre. In such a situation, a surplus of either Cl^- or $SO_{4^{2-}}$ co-anions derived from the added NaCl or Na_2SO_4, respectively, will remain in the dyebath phase, which cannot be rationalised mechanistically, since electrical neutrality must of course be conserved at all times within the anionic dye(dye precursor)/inorganic electrolyte/cellulosic fibre system.

Furthermore, the suppression of negative surface charge hypothesis dictates that the surplus Cl^- or $SO_{4^{2-}}$ electrolyte-derived anions in the dyebath phase take no part at all in the dyeing process, as they are assumed to exert neither a promotional effect nor a restraining effect upon anionic dye uptake: for example, Equation 1 takes no cognisance of electrolyte-derived anions. It can be anticipated that the small molecular size and highly mobile Cl^- or $SO_{4^{2-}}$ ions will indeed be unlikely to compete with their considerably larger, considerably much higher substantivity, dye/dye precursor anions (e.g. D-SO_{3^-}) in terms of adsorption onto the electrically 'neutralised' fibre surface. However, the Cl^- or $SO_{4^{2-}}$ ions within the dyebath phase will unquestionably impart dramatic effects to the extensive, three-dimensional, H-bonded structure of water, as well as the state of aggregation and consequent solubility of the anionic dye/dye precursor anions present in the aqueous dyebath. In the latter context, the well-known

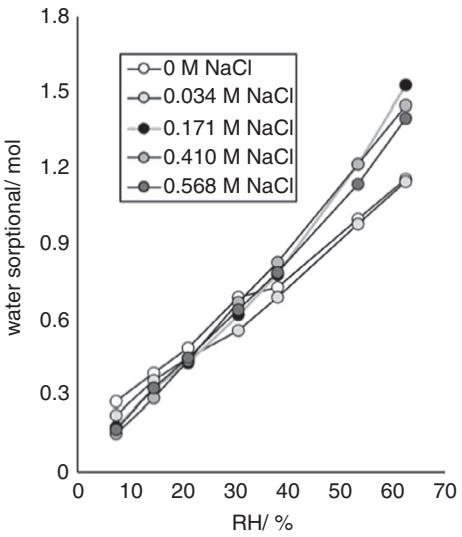

FIGURE 16 Effect of sorbed NaCl on water sorption of CV sheet at 25°C; drawn using data from[16]

and often quite remarkable effects that electrolyte anions, such as Cl^- or $SO_{4^{2-}}$, impart to water structure and the solubility of many types of dissolved/dispersed molecules,

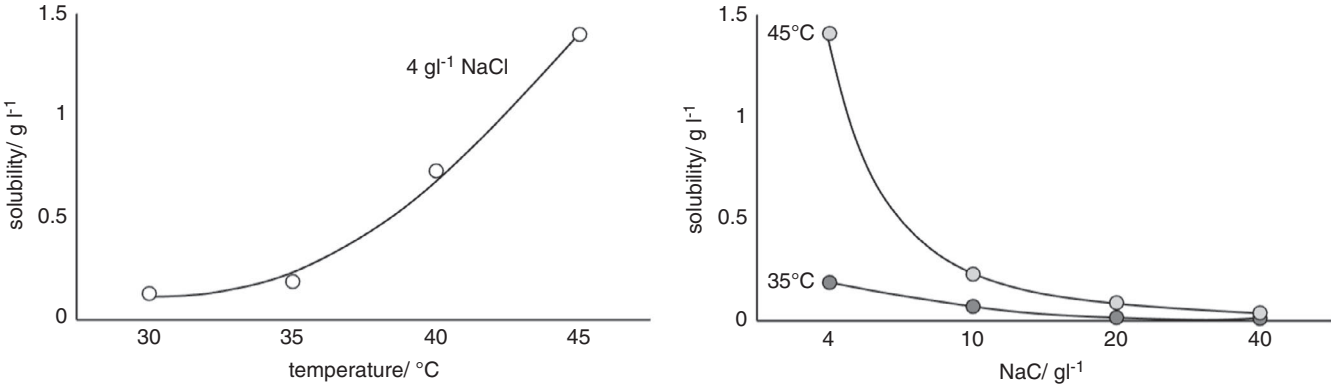

FIGURE 17 Effect of NaCl and temperature on the solubility of purified C.I. Direct Yellow 12; drawn using data from[162]

is a much studied topic as represented by the concepts of structure-making/structure-breaking ions, kosmotropes and chaotropes, salting-in and salting-out, the Hofmeister series, etc., discussed in section 4.

5.2 | Increased water sorption

A less commonly cited theory of the role of added inorganic electrolyte in cellulosic fibre dyeing, which invokes a view of electrolyte-fibre interactions that differs to the notion of surface charge neutralisation, is that the added NaCl or Na_2SO_4 increases the amount of water sorbed by the substrate. For example, Neale *et al*[16] demonstrated that inorganic electrolyte increased the amount of water imbibed by CV sheet (Figure 16).

Curiously, Figure 16 shows that a somewhat diffuse relationship is obtained between the extent of increased water sorption imparted by NaCl and the concentration of the aqueous NaCl solution used. Also, whilst the extent of increased water uptake imparted by the inorganic electrolyte was greatest at the highest value of Relative Humidity *(RH*) studied (i.e. 65% *RH*), the extent of increased water uptake was not especially marked across the overall range of relative humidity considered. Moreover, the effects of different amounts of NaCl on the extent of water sorbed under aqueous conditions typically encountered in exhaust dyeing process, namely at the *saturation value* of the CV substrate (i.e. at 100% *RH*) were not presented. As such, the hypothesis that the promotional effect imparted to anionic dye uptake by added inorganic electrolyte can be attributed to increased water sorption within the cellulosic substrate is not especially convincing.

5.3 | Increased specific volume

In a related vein, the previously discussed (section 2) observation[16] that inorganic electrolytes, including NaCl, increased the specific volume of cellophane (Figure 4), which has implications for the value of the internal volume, *V*, of cellulosic substrates that is employed in equations such as Equation 1, can be considered as another theory of the role of added NaCl or Na_2SO_4 on anionic dye uptake that involves electrolyte-fibre interactions. However, as also recounted in section 2, because neither the precise nature of the internal volume of cellulosic substrates nor the magnitude of this elusive and poorly defined substrate-related parameter have been satisfactorily resolved, the possible relevance of the observed increase in cellulosic substrate specific volume imparted by inorganic electrolyte, as depicted in Figure 4, to the role of inorganic electrolyte in dyeing is unclear.

This somewhat brief analysis of the possible contribution that inorganic electrolyte-cellulosic fibre interactions potentially make to the promotional role of added inorganic electrolyte in cellulosic fibre dyeing using anionic dyes, suggests that suppressed dye-fibre electrical repulsion, as well as electrolyte-induced increased water sorption and increased fibre specific volume are not primary contributing factors. Although these various inorganic electrolyte-fibre effects may well make some, though limited, contribution, to the remarkable promotional impact of added NaCl or Na_2SO_4 on anionic dye uptake, it can be concluded that some other type(s) of electrolyte-induced effect(s) is/are the principal contributing factor(s). In the latter context, as discussed below, the most likely of candidates involve electrolyte-dye interactions.

6 | ELECTROLYTE-DYE INTERACTIONS

Sadly, relatively few accounts are available that concern the effects of inorganic electrolyte on the solubility of anionic dyes, probably because of inherent experimental difficulties involved in determining dye solubility in electrolyte solutions.[22] Indeed, aqueous dye solubility in general has received surprisingly little interest, attention being principally focussed on that of disperse dyes.[145-158]

Nonetheless, the remarkable ability of NaCl or Na_2SO_4 to reduce the aqueous solubility of direct dyes, which typically ranges from ~5 to 200 g l^{-1} in the absence of electrolyte at 98°C,[159] is illustrated by the data displayed in Figure 17; the temperature dependency of the NaCl-induced reduction in dye solubility is also evident.

Likewise, reactive dyes characteristically display very high levels of aqueous solubility (e.g. solubility/g l^{-1}: C.I. Reactive Blue 2, 60; C.I. Reactive Red 4, 120; C.I. Reactive Yellow 2, 70 at 25°C;[160] C.I. Reactive Blue 19, 100; C.I Reactive Red 198, 70 at 20°C[161]) that is reduced in the presence of inorganic electrolyte, as demonstrated by the *Novacron FN* (Huntsman) commercial range of dyes, for which aqueous solubility is reduced from 100 g l^{-1} in water at 60°C to 30 g l^{-1} in the presence of 60 g l^{-1} aqueous electrolyte at 60°C.[141]

The reduction in dye solubility imparted by inorganic electrolytes, which can be quite considerable, as demonstrated by the data presented in Figure 17, varies according to both the nature and concentration of the polar dye molecule under consideration (e.g. planarity, number and type of solubilising groups, etc.) and that of the particular inorganic electrolyte(s) involved (e.g. structure maker/breaker type ion, valency, ion size, etc.), as well as characteristics of the aqueous environment (e.g. pH, temperature, ionic strength, etc.). In terms of a typical aqueous dyebath used for cellulosic fibre dyeing, it therefore follows that the likely influence which inorganic electrolytes, such as NaCl or Na_2SO_4, impart to dye solubility, will vary according to not only the particular nature of the dye/dye precursor anion [i.e. phenolate, Ar-O^- (azoic coupling component), enolate, -C-O^- (vat dye), sulfonate, -SO_3^- (direct dye and reactive dye) or thiolate, -S^-, (sulphur dye)] but also the composition of the particular dyebath (e.g. pH, temperature, presence of reductants, ionic strength, etc.).

Such a situation is reflected in the fact that, as previously discussed,[1] a diverse range of application conditions (pH, temperature, etc.) are employed for vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes, owing to the sizeable, structure-related and property-related (solubility, functional group content, etc.) differences exhibited by the different dye classes. It is therefore not surprising that the amount of added inorganic electrolyte required for immersion application varies for the five types of dye under consideration (Figure 11).

6.1 | Dye self-association

Most classes/types of dye display a distinct inclination to *self-associate*, with the result that *dye particles* are often formed that comprise aggregates of dye molecules. Indeed, because dye aggregation is so commonly encountered in all dye/fibre systems, it can be considered to be a general characteristic property of a dye.[163,164]

Although dye aggregation in solution has enjoyed considerable attention over many decades, principally because of its relevance to several areas of science and technology,[22,163-176] in contrast, dye aggregation within solid substrates has received comparatively much less interest owing to inherent experimental challenges and, in the case of (solid) textile fibres, has mostly focused on studies related to dye photofading.[177-179]

The intermolecular forces of attraction that contribute to dye self-association can be considered to include van der Waals forces, H-bonding, π-π interactions and hydrophobic interaction,[180] though the precise nature of the attractive intermolecular forces responsible for the phenomenon will likely vary according to the particular structural characteristics of a given class/type of dye.[22] In essence, the aggregation of all types of dye is a stepwise process in which dye *monomers* initially associate to form *dimers* that grow by association of additional monomers, via *trimers*, *tetramers*, etc., in which planar dye molecules/ions stack progressively in such a manner that π-π interactions between aromatic centres in adjacent dye molecules/ions are maximised and electrostatic interactions between charged groups (e.g. -SO_3-) are minimised.[22]

Dye self-association can therefore be considered to be a characteristic feature of vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes, because of their pronounced *amphiphilicity*, namely presence of hydrophilic groups (e.g. -SO_3Na, -NH_2, =C-OH, etc.) attached to non-polar moieties (e.g. planar aromatic rings), together with an inherent predisposition to undergo *coplanar association* which stems from their characteristic planar structure. Consequently, each of the five types of dye/dye precursor molecule displays an innate tendency to aggregate, both in solution within the dyebath phase and in the (solid) fibre phase.[22]

The extent of aggregation observed for various classes/types of dye is known to depend on several factors, being influenced by various physical and chemical attributes of the surrounding environment, insofar as, aggregation increases with decreasing temperature, reduced liquor ratio (which is equivalent to increased dye concentration) and, of relevance to this paper, the presence of inorganic electrolyte. In the latter context, inorganic electrolyte has been observed to promote both the rate and extent of aggregation of various classes of dye in solution,[181-187] although as might be anticipated, different classes/types of dye (e.g. non-metallised acid dyes, pre-metallised acid dyes, basic dyes, direct dyes, etc.) vary, widely, in terms of their electrolyte-sensitivity, owing to both structural and physical property variations (e.g. chromogen type, number and types of functional group, etc.).

From the perspective of the five dye classes used for cellulosic fibre dyeing, studies of electrolyte-induced aggregation

have focussed predominantly on direct dyes[158,188-197] and reactive dyes[198-204]]. For example, the extent of aggregation of direct dyes increases with increasing amount of inorganic electrolyte, as illustrated by the data presented in Figure 18.

In a similar manner, Figure 19 shows the effects of increasing amounts of NaCl on the state of aggregation of a triphenodioxazine reactive dye in solution, as expressed in terms of the molar fraction of the monomeric and dimeric forms of the dye. It is apparent that dimerisation is promoted by an increase in NaCl concentration and also increases with increasing dye concentration (Figure 19).

The promotional effect imparted by inorganic electrolytes to anionic dye aggregation, such as that illustrated by the data presented in Figures 18 and 19, can be explained in terms of a *screening effect*, which parallels that of *electric double-layer theory* (section 5.1), in which the thickness of the double layer (i.e. the Debye length, κ^{-1}) that surrounds a charged species located within an ionic environment within a polar liquid, such as water, when it is in the close proximity of a charged surface, such as a textile fibre, is reduced in the presence of electrolytes.[22] As recently articulated in the case of direct dyes on cotton,[44] the remarkable ability of added NaCl or Na_2SO_4 to promote the self-association of the anionic dyes can be attributed to electrolyte-derived Na^+ cations screening the ionised -SO_{3-} groups carried by the dye molecule, which suppresses the extent of ionisation of the dye solutes so that the ensuing direct dye molecules possess lower solubility within the aqueous dyebath phase. Moreover, because the screening effect of the Na^+ counterions reduces the anionicity of the direct dye molecules, the extent of electrostatic repulsion operating between adjacent direct dye anions will be reduced, which encourages hydrophobic, π-π interactions between aromatic regions in neighbouring dye molecules, thereby favouring dye aggregation. Such hydrophobic interaction can be assumed to be encouraged by the surrounding water molecules seeking to minimise their contact with the solute molecules by forcing them out of solution, so as to satisfy the intrinsic requirement of water molecules to preserve the extensive H-bonded structure of liquid water.[205]

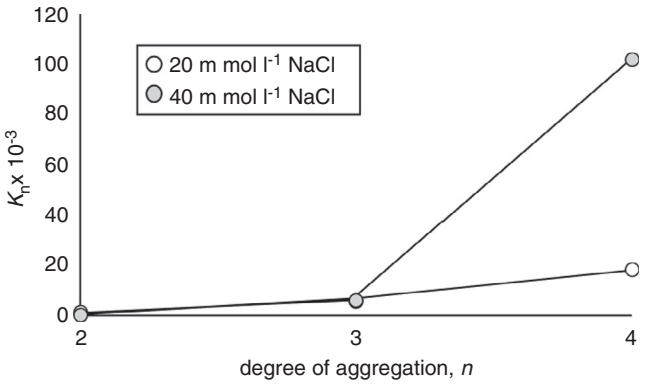

FIGURE 18 Effect of inorganic electrolyte concentration on equilibrium constant of aggregation, K_n, of C.I. Direct Red 2; drawn using data from[188]

It can therefore be considered[44] that in the case of direct dyes, the electrolyte-derived Na^+ cations function as *kosmotropes* insofar as, the small size, high charge density cations bind water molecules, which expedites hydrophobic dye-dye interaction, thereby promoting aggregation and stabilising the resulting dye particles. This particular mechanism of electrolyte-induced dye aggregation supports the views expressed by several workers that hydrophobic interaction plays a major role in dye self-association in solution.[22,206-208]

As an identical screening effect mechanism was proposed to explain the promotional effect exerted by added inorganic electrolyte ions on the sulfonate anions, -SO_{3-}, (and other types of anionic group) carried by reactive dyes[209] which are applied to cellulosic fibres, it seems reasonable to propose that this mechanism can be expected to apply to the phenolate anions, Ar-O^-, carried by alkali-solubilised azoic coupling components, as well as both thiolate, -S^-, and enolate, -C-O^-, anions, respectively, in the cases of leuco sulphur dyes and leuco vat dyes.

Dye self-association can be expected to occur during each of the two-stages that are involved in the exhaust application of vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes, to cellulosic fibres. By way of explanation, as recounted in the first part of the paper,[1] the first stage of applying each of these five classes of dye involves the transfer of the dissolved dye/dye precursor anion, namely phenolate (Ar-O^-: azoic coupling component), enolate (-C-O^-: vat dye), sulfonate (-SO3$^-$: direct dye and reactive dye) or thiolate (S^-,: sulphur dye) derivative, respectively, through the aqueous dyebath to water-filled, swollen, amorphous domains located within the semi-crystalline cellulose polymer. The sorbed dye/dye precursor anions then eventually interact with appropriate -OH groups located within the constituent cellulose polymer chains and become adsorbed onto the cellulosic substrate [for discussions of anionic dye/cellulose interactions see for example 210-222], because the electrolyte-derived Na^+ cations screen the anionic groups (Ar-O^-, -C-O^-, etc.) carried by each type of dye, which encourages the phenolate, enolate, etc. derivative to aggregate. The fact that different amounts of added inorganic electrolyte are employed to apply the five dye classes to a given type of cellulosic fibre (Figure 11) can be considered to reflect the relative sensitivity of each anionic dye variant (e.g. phenolate, enolate, etc.) towards NaCl or Na_2SO_4, and, therefore, the interrelated electrolyte-induced self-association character of each type of anionic dye variant.

In effect, the variable, electrolyte-dependent nature of each the five types of dye, as expressed in terms of the relative amount of NaCl required for application (Figure 11), can be considered to echo the relative anionicity of each type of dye variant (phenolate, enolate, etc.), which, by extension,

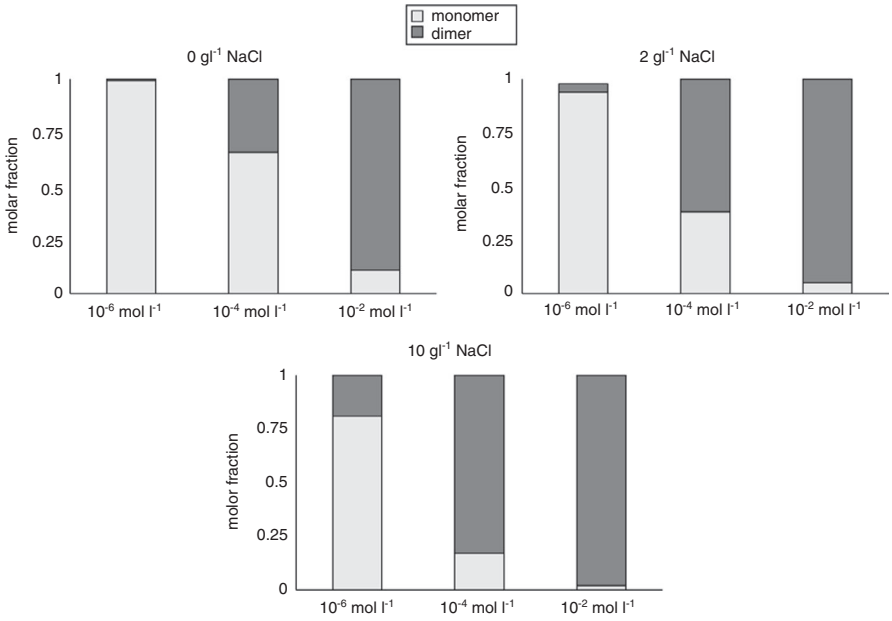

FIGURE 19 Effect of increasing amount of NaCl and increasing dye concentration on the molar fraction of the monomeric and dimeric forms of a triphenodioxazine reactive dye in aqueous solution at 25°C; drawn using data from[202]

can be considered to reflect the relative solubility of each type of dye anion under the particular dyebath conditions employed. Thus, as discussed below, the fact that different amounts of added inorganic electrolyte are typically used to apply vat dye, sulphur dye, azoic coupling component, direct dye and direct dye anions to cotton (Figure 11) and other types of cellulosic fibre stems from the fact that the anionic dye/dye precursors display different levels of solubility within the particular dyebaths that are utilised for their exhaust application.

The second stage of applying the five dye classes involves the in situ generation of the insoluble azo compound (OH-Ar-N=N-Ar') in the case of azoic colorants, the re-generation of the insoluble enol variant (-C-OH) of vat dyes and the conversion of the thiolate derivative of sulphur dyes to the lower solubility disulfide (-S-S-) and/or oligosulfide ($[-S-S-]_n$) variant, as well as the formation of dye-fibre covalent bonds in the case of reactive dyes and the self-association of direct dyes. It therefore follows that during each of these crucially important, second-stage, in situ processes, the amphiphilic, planar structure of the ensuing azoic colorant, vat dye, sulphur dye, etc. molecule means that each dye type will exhibit a distinctive tendency to aggregate, which will be encouraged by the presence of added inorganic electrolyte.

In support of this latter proposal, whilst the aggregation of dyes within fibres has received comparatively much less scrutiny than that in aqueous solution owing to experimental difficulties, the presence of dye aggregates has been detected within various types of cellulosic fibre in the cases of vat dyes, azoic colorants, direct dyes and reactive dyes.[177,202,213,223-227] Indeed, the intrinsic disposition of vat dyes to self-associate in situ within dyed cellulosic fibres, which stems from the marked amphiphilic and planar structural characteristics of the adsorbed vat dye molecules, is most likely responsible for the well-known shade stabilisation effects that occur during the '*soaping*' stage of the leuco vat dyeing process,[225] though alternative explanations for these phenomena[228,229] have been proposed.

Therefore, whilst vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes differ considerably in terms of their structure, physico-chemical properties and the conditions utilised for their application to cellulosic fibres,[1] the five dye classes share the same, crucially important structure-dependent characteristic, namely, that added NaCl or Na_2SO_4 promotes dye uptake by reducing the solubility of the respective, highly water-soluble anionic variant which thereby exploits the intrinsic tendency of the amphiphilic, planar dye molecules to self-associate both in the aqueous dyebath and within the amorphous domains that reside in the cellulosic substrate, as proposed in the case of direct dyes[205] and reactive dyes.[209]

6.2 | Combined reduced dye solubility/ increased dye self-association

From a consideration of the phenomenon of inorganic electrolyte-induced dye self-association, it was concluded[44] that NaCl or Na_2SO_4 exerts a two-stage promotional effect on both direct dye and reactive dye uptake in that added electrolyte reduces the solubility of the direct dye or reactive dye anions and also increases the inherent disposition of the dye molecules to aggregate. However, the precise reasons *why* the combination of inorganic electrolyte-induced reduced dye solubility and enhanced dye aggregation impart increased dye-fibre substantivity and therefore result in increased dye/dye precursor uptake on cellulosic fibres, merit consideration.

Liquor ratio	Volume of dyebath water/cm^3	Interstitial water volume/cm^3	Bulk water volume/cm^3
1:1	1000	220	780
1:2	2000	220	1780
1:3	3000	220	2780
1:5	5000	220	4780
1:10	10,000	220	9780
1:20	20,000	220	19,780

TABLE 3 variation of interstitial water volume and bulk water volume as a function of liquor ratio in the case of 1 kg of cotton assuming saturation moisture regain of cotton is ~0.22 l kg^{-1}

In essence, the fundamental hypothesis of this combined reduced dye solubility/increased dye aggregation model is entirely counter-intuitive as it assumes that in the presence of added inorganic electrolyte, the amount of dissolved direct dye or reactive dye molecules present in the aqueous dyebath will *decrease* because of the joint effects of increased dye aggregation and reduced dye solubility. However, it follows that if such a situation were to occur then the *amount* of direct dye or reactive dye in the dyebath available for adsorption onto the fibre would therefore decrease rather than increase, because of the lower amount of dissolved direct dye and reactive dye anions present in the aqueous dyebath phase. Thus, added inorganic electrolyte should decrease rather than increase the extent of direct dye or reactive dye uptake.

This particular mechanistic shortcoming was recently addressed in a series of studies that sought to examine the role of inorganic electrolyte in the dyeing of cotton using both direct dyes and reactive dyes,[25,26,44,45,205,209,230-233] which resulted in models of direct dye and reactive dye adsorption being proposed.[205,209] According to these models, added NaCl or Na_2SO_4 reduces the aqueous solubility of the dye and promotes dye self-association in the dyebath phase, so that the innate predisposition of the previously highly soluble direct dye or reactive dye to favour the aqueous dyebath phase shifts towards the fibre phase and, therefore, dye uptake is promoted. In effect, the combined effects of reduced dye solubility and enhanced dye aggregation reduce the tendency of the dyes to prefer the aqueous dyebath phase which results in the dye being encouraged to transfer to the solid fibre.

As these models of direct dye and reactive dye adsorption on cotton[205,209] invoked the concept of *interstitial water in dyeing*, a brief discussion of this theory, from the viewpoint of its relevance to cellulosic fibre dyeing, seems appropriate.

6.3 | Interstitial water in dyeing

According to this concept, which has been utilised to develop an ultra-low liquor ratio exhaust dyeing process for various dye-fibre systems[234] and wash-off processes for dyeings,[235-238] the term *interstitial water* refers water that has been adsorbed by a textile fibre and which resides within

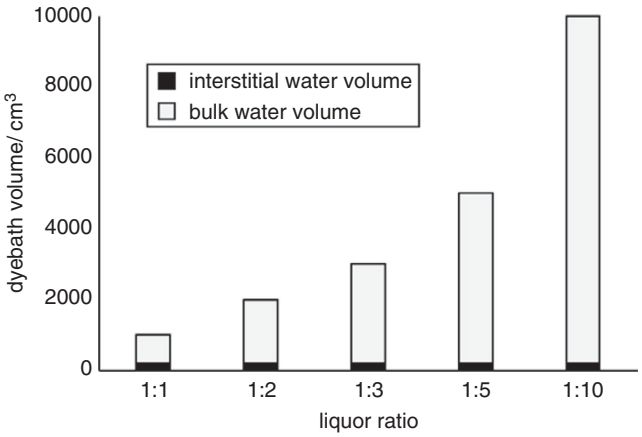

FIGURE 20 Constancy of interstitial water volume as a function of liquor ratio in the case of 1 kg of cotton assuming saturation moisture regain of cotton is ~0.22 L kg^{-1}; plotted using data from Table 3

the *interstitial volume* (or *interstitial space*) that exists between constituent polymer macromolecules located within the amorphous domains of the substrate.[22]

Interstitial water therefore constitutes only a very small proportion of the water that is utilised in an exhaust dyeing process. It corresponds to sorbed water that is required to saturate the fibre and impart the crucially important functions of *water-induced fibre swelling* and *water-induced fibre plasticisation* which are necessary to enable the diffusion and adsorption of dye molecules within textile materials.[1,22] The amount of interstitial water therefore corresponds to the substrate's moisture regain at 100% *RH*,[22] which vary for different types of fibre (e.g. saturation moisture regain/ %: CV 0.46; cotton 0.22;[23] PA 66 8.5-8.8[239]). The remaining vast majority of the water employed in exhaust dyeing processes is referred to as *bulk water*,[235] which is not adsorbed by the fibrous substrate, but, instead, resides within the bulk aqueous dyebath that surrounds the wetted fibrous substrate, and provides several vital functions such as mechanical interaction, dye dispersion/dissolution, thermal interchange, etc.[22]

By way of brief example, as the saturation moisture regain of cotton is of the order ~0.22 l kg^{-1},[3] it follows that when 1 kg of cotton is immersed in 5 l of water (corresponding to

a 1:5 liquor ratio), the volume of interstitial water is 220 cm^3 and that of the surrounding bulk water 4780 cm^3 (Table 3).

As interstitial water is a (measurable) physical attribute of a particular fibre (i.e. the substrate's moisture regain at 100% *RH*), so the amount of interstitial water remains constant, irrespective of the liquor ratio employed for dyeing, as illustrated by the data presented in Table 3 and Figure 20.

Both models of the direct dyeing and reactive dyeing of cotton that invoked the concept of interstitial water in dyeing[205,209] assume that the aqueous dye solution which is present within the interstitial regions of the fibre is equivalent to that which resides within the bulk dyebath that surrounds the substrate in terms of composition and properties; it is also assumed that interstitial water and bulk water are in a state of constant interchange.[235]

It is further assumed that when, for example cotton (saturation moisture regain ~0.22 l kg^{-1}) is immersed in, say, 5 l of an aqueous direct dye dyebath, the interstitial regions of the water-swollen, water-plasticised substrate will contain 0.22 l of *interstitial dye solution*, d_{int}, the remaining vast majority of the dyebath, namely 4.78 l, being present in the form of a *bulk dyebath dye solution*, d_{sol}, and a bulk *dyebath dye dispersion*, d_{disp}, that surrounds the cotton fibre.

In order to expound this mechanism, a simple mathematical expression was derived to describe the effect of added inorganic electrolyte on the substantivity of the direct dye or reactive dye molecules towards the cellulosic fibre.[205,209] Such an approach contrasts to that adopted in conventional thermodynamic and kinetic analyses of equilibrium dye adsorption data, discussed in section 3, as it does not necessitate the collection and utilisation of experimentally determined dye adsorption data.[205,209] Instead, the approach employed was conceptual in nature, seeking to describe in general, *quantitative terms*, the variously observed and reported promotional effects imparted by added NaCl or Na_2SO_4 to direct dye and reactive dye uptake.

For simplicity, the following interpretation of this mathematical approach [205,209] relates to the effect of added inorganic electrolyte on the uptake of direct dyes on cotton.

The total amount of dye within a direct dye/inorganic electrolyte/cotton fibre system, $[D]$, consists of dissolved monomolecular direct dye anions that reside within the interstitial dye solution located in the fibre phase, $[d_{int}]$, together with dissolved dye molecules that are present in the bulk dyebath dye solution, $[d_{sol}]$, as well as both low solubility dye aggregates and low solubility dye particles that are present within the bulk dyebath dye dispersion, $[d_{disp}]$. Such a situation is represented by Equation 3, from which Equation 4 can be written.

$$[D] = [d_{int}] + [d_{sol}] + [d_{disp}] \quad (3)$$

$$[d_{int}] = [D] - [d_{sol}] - [d_{disp}] \quad (4)$$

According to Equation 4, the amount of dissolved monomolecular direct dye anions that reside within the interstitial dye solution located in the fibre phase, $[d_{int}]$, depends on the proportion of dye that is present in the bulk dyebath dye solution, $[d_{sol}]$, and bulk dyebath dye dispersion, $[d_{disp}]$, relative to the total amount of dye within the dyeing system, $[D]$.

Added NaCl or Na_2SO_4 reduces the aqueous solubility of the dye in the dyebath phase, which promotes dye self-association in the dyebath phase. As a consequence of these two electrolyte-induced effects, the magnitude of $[d_{sol}]$ will decrease and that of $[d_{disp}]$ will increase, correspondingly, so that the innate predisposition of the previously highly soluble direct dye to favour the aqueous dyebath phase shifts towards the fibre phase so that dye uptake is promoted and, therefore, $[d_{int}]$, increases.

The relative distribution of the direct dye between the dyebath phase and the fibre phase at a given point in an exhaust dyeing process can be represented by Equation 5 where $[D]_f$ is the amount of dye present in the fibre phase, *f*, relative to the amount of fibre and $[D]_s$ the amount of dye in the dyebath (i.e. in solution), *s*, relative to the amount of solution. In this case, *K*, the *partition coefficient* describes the relative distribution of the dye between the fibre phase and the solution phase.

$$K = \frac{[D]_f}{[D]_s} \quad (5)$$

High values of *K* indicate that the distribution of the dye favours the fibre phase (i.e. $[D]_f > [D]_s$) and, therefore, the greater is the extent of dye uptake onto the substrate.

According to the interstitial models of the direct dyeing and reactive dyeing of cotton,[205,209] the aqueous dyebath phase comprises *bulk dyebath dye solution*, d_{sol}, and bulk *dyebath dye dispersion*, d_{disp}, whilst the fibre phase comprises *interstitial dye solution*, d_{int}. Equation's 6 and 7 therefore apply, so that Equation 5 can be written in the form of Equation 8 from which it is apparent that the ratio $[d_{int}]/[d_{sol}] + [d_{disp}]$ describes the relative partition of the dye between the fibre phase, $[D]_f$, as expressed in terms of $[d_{int}]$, and the dyebath phase, $[D]_s$, expressed in terms of $[d_{sol}]$ and $[d_{disp}]$. Equation 8 therefore describes the relative extent of dye uptake onto the substrate: the higher the value of this ratio so the partition of the dye more favours the fibre phase and the greater is the extent of dye uptake onto the cotton substrate.

$$[D]_f = [d_{int}] \quad (6)$$

$$[D]_s = [d_{sol}] + [d_{disp}] \quad (7)$$

$$K = \frac{[d_{int}]}{[d_{sol}] + [d_{disp}]} \quad (8)$$

By way of simple illustration, Table 4 shows that values of the dyebath parameters $[d_{sol}]$ and $[d_{disp}]$ assumed for a fictitious direct dye applied at 5% omf (i.e. $[D] = 50$) to an equally fictitious cellulosic substrate vary, as a function of the amount of added NaCl present in the dyebath. In Table 4, the amount of inorganic electrolyte is assumed to increase in a simple, linear manner over the range 0 to 10 g l^{-1}. In a similar manner, the proportion of dissolved direct dye molecules within the dyebath dye solution, $[d_{sol}]$, and that of both low solubility dye aggregates and dye particles present within the dyebath dye dispersion, $[d_{disp}]$, are also each assumed to vary in a simple manner, as a function of the amount of NaCl in the dyebath.

When the values of $[d_{sol}]$ and $[d_{disp}]$ in Table 4 are plotted as a function of NaCl in the dyebath, Figure 21 is obtained. It is apparent that as the amount of NaCl present in the direct dyebath phase increases, the solubility of the dye decreases, which results in a decrease in the proportion of dissolved dye molecules that are present in the bulk dyebath dye solution, $[d_{sol}]$ and, as a corollary, the proportion of both low solubility dye aggregates and dye particles present within the bulk dyebath dye dispersion, $[d_{disp}]$, increases.

Using Equation 4 and the values of $[d_{sol}]$ and $[d_{disp}]$ in Table 4 enables the corresponding values of $[d_{int}]$ to be determined, which are plotted as a function of the amount of NaCl in the dyebath in Figure 22.

The increase in the extent of dye uptake, as represented by $[d_{int}]$, as a function of the amount of NaCl in the dyebath phase (Figure 22), is attributable to a corresponding decrease in the solubility of the dye, as expressed by the proportion of dissolved dye molecules present in the bulk dyebath dye solution, $[d_{sol}]$.

Equation 8 enables the effect of added NaCl on the relative distribution of the dye between the fibre phase and the dyebath phase to be established; Figure 23A shows the resulting inorganic electrolyte-dependency of partition coefficient, K.

TABLE 4 Simple representation of variation of dyebath parameters $[d_{sol}]$ and $[d_{disp}]$ as a function of increasing amounts of NaCl present in the dyebath, for a fictitious direct dye/cellulosic fibre system; $[D] = 50$

NaCl/g l^{-1}	$[d_{sol}]$/g l^{-1}	$[d_{disp}]$/g l^{-1}
0	47	2
1	44	3
2	39	6
3	35	9
4	29	12
5	24	15
6	19	18
7	14	21
8	9	24
9	4	27
10	1	30

From the upward sloping plot of K as a function of the amount of NaCl in the dyebath phase presented in Figure 23A, Equation 8 predicts that the partition of the fictitious direct dye towards the fictitious cellulosic fibre between the dyebath and fibre phases increases with increasing amount of NaCl in the dyebath. Whilst this finding is to be anticipated since the extent of dye uptake, as expressed in terms of $[d_{int}]$, increases with increasing amount of inorganic electrolyte (Figure 22), of significance is the fact that the profile of the upward sloping curvilinear plot of K versus dyebath concentration of NaCl shown in Figure 23A, which of course is a consequence of the assumed variation of $[d_{sol}]$ and $[d_{disp}]$ employed (Table 4), is similar to those secured in equilibrium adsorption studies of the direct dye/inorganic electrolyte/cellulosic fibre system, as illustrated by the plot displayed in Figure 23B, in which the values of K were calculated using Equation 5, employing the equilibrium adsorption data secured for C.I Yellow 12 on CV at 40°C,[24] that were presented earlier in Figure 5.

In terms of the relative comparability of Figure 23A,B, a brief discussion of the nature of K seems appropriate. Because the amount of fibre used in immersion dyeing processes is measured as a mass unit (e.g. kg) and the amount of dyebath is expressed as a volume unit (e.g. l), the units employed for $[D]_f$ are, for example, g kg^{-1} and those of $[D]_s$ are, for example, g l^{-1}. In order to ensure values of the partition constant, K, determined using Equation 5, are *dimensionless*, the same units must be adopted for experimentally determined values of both $[D]_f$ and $[D]_s$, for example in mass terms (e.g. g kg^{-1}) or volume terms (e.g. g l^{-1}). Alternatively, values of $[D]_f$ can be divided by an assumed value of the fibre parameter *internal volume*, V (section 3.1) as values of V are expressed in volume terms, such as g l^{-1}, which resolves the issue of division by unlike units, so that values of K in Equation 5 are dimensionless. The latter approach was adopted by the author of the data used in Figure 23B, insofar as values of $[D]_f$ were divided by an assumed value of 0.33 g l^{-1} for the internal volume, V, of the cellophane substrate employed.[24] In the case of Equation 8, no such mathematical adjustment is required since the same units, namely g l^{-1}, are used for the variables $[d_{int}]$, $[d_{sol}]$) and $[d_{disp}]$.

The fact that similar upward sloping plots are secured when hypothetical values of the dyebath parameters $[d_{sol}]$) and $[d_{disp}]$ and the dyebath parameter $[d_{int}]$, were employed in the case of the fictitious direct dye/fictitious cellulosic fibre system using Equation 8 (Figure 23A) and non-hypothetical, experimentally determined values of $[D]_f$ and $[D]_s$ secured for a direct dye/cellophane system were employed in Equation 5 (Figure 23B), is again to be anticipated, since Equation 8 is derived from Equation 5 and $[d_{int}]$, $[d_{sol}]$) and $[d_{disp}]$ are related to $[D]_f$ and $[D]_s$, respectively, via Equations 6 and 7.

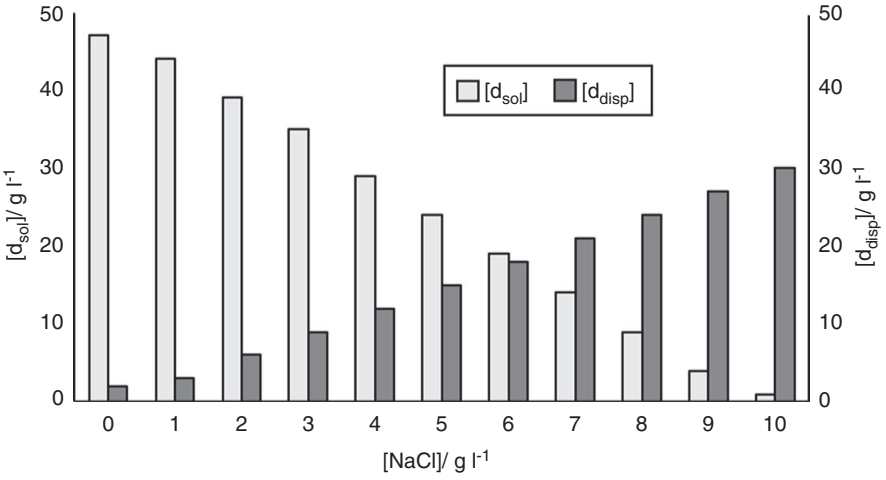

FIGURE 21 Variation of $[d_{sol}]$ and $[d_{disp}]$ for a fictitious direct dye/cellulosic fibre system as a function of the amount of added inorganic electrolyte present in the dyebath; plotted using the data in Table 4

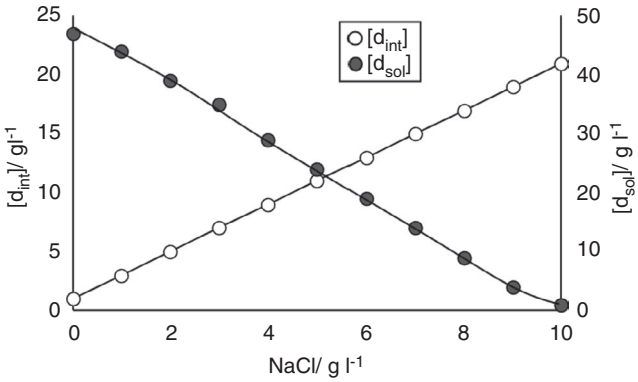

FIGURE 22 Variation in dye uptake, $[d_{int}]$, predicted by Equation 4 and the proportion of dissolved dye molecules present in the bulk dyebath dye solution, $[d_{sol}]$, as a function of amount of NaCl in the dyebath phase, for a fictitious direct dye/NaCl/cellulosic fibre system

What is interesting about the comparability of the K versus amount of NaCl plots displayed in Figure 23A,B is that the interstitial models of direct dyeing (and reactive dyeing) of cotton[205,209] expressed in the form of Equation 8, not only predict that values of K should increase with increasing amounts of added inorganic electrolyte (Figure 23A) but, more importantly, offer a possible explanation as to *why* the extent of direct dye uptake, as interpreted via K, will increase with increasing amounts of NaCl in the dyebath. As previously articulated, according to the interstitial models of direct dyeing and reactive dyeing of cotton [205,209] the reasons why K increases with increasing amount of NaCl in the dyebath (Figure 23A) is because added inorganic electrolyte reduces the aqueous solubility of the dye and promotes dye self-association in the dyebath phase, so that the innate predisposition of the previously highly soluble direct dye or reactive dye to favour the aqueous dyebath phase shifts towards the fibre phase and, therefore, dye uptake is promoted.

The interstitial models of the direct dyeing (and reactive dyeing) of cotton,[205,209] as interpreted via the simple arithmetic expression presented in Equation 8, are therefore able to account for, in very general, quantitative terms, the promotional effects imparted by added NaCl or Na_2SO_4 to the uptake of these two types of anionic dye on cotton. In this context, Equation 8 therefore provides a possible explanation of the mechanism by which added inorganic electrolyte promotes direct dye (and reactive dye) uptake on cellulosic fibres, which, as discussed in section 3, is something that none of the myriad qualitative thermodynamic and kinetic mechanistic studies of anionic dye/inorganic electrolyte/cellulosic fibre systems, as exemplified by the findings displayed in Figures 1, 2, 4 and 5, is intrinsically incapable of doing.

Moreover, Equation 8 does not necessitate the collection of copious amounts of experimentally determined dye adsorption/diffusion data and their complex mathematical analysis nor via the adoption of some or other mechanism of dye-fibre adsorption (i.e. Freundlich-type of Langmuir-type) in order to explain how added inorganic electrolyte promotes dye uptake. Of course, in reality, the extent of dye uptake achieved, as expressed by $[d_{int}]$, will be the consequence of various characteristics of the particular direct dye/inorganic electrolyte/cellulosic fibre system under consideration, which will combine so as to furnish an overall mechanism of dye adsorption which can be described in terms of, for example, a Freundlich-type or Langmuir-type process (section 3).

As such, Equation 8, and the ensuing $[d_{int}]$ vs [NaCl] plot presented in Figure 22 and the upward sloping K versus {NaCl] plot in Figure 23A, simply attempts to propose that the manner by which added inorganic electrolyte promotes direct dye uptake, is dominated by the solubility of the dye in the dyebath phase. The interstitial models of the direct dyeing and reactive dyeing of cotton,[205,209] as represented by Equation 8, therefore predict that the preference of the high solubility, direct dye to favour the interstitial dye solution in the fibre phase, $[d_{int}]$, increases as the solubility of the dye in the dye solution in the dyebath phase, $[d_{sol}]$, decreases.

The characteristic low substantivity displayed by direct dyes towards cotton in the absence of added NaCl or Na_2SO_4 can therefore be attributed to the dye's intrinsically

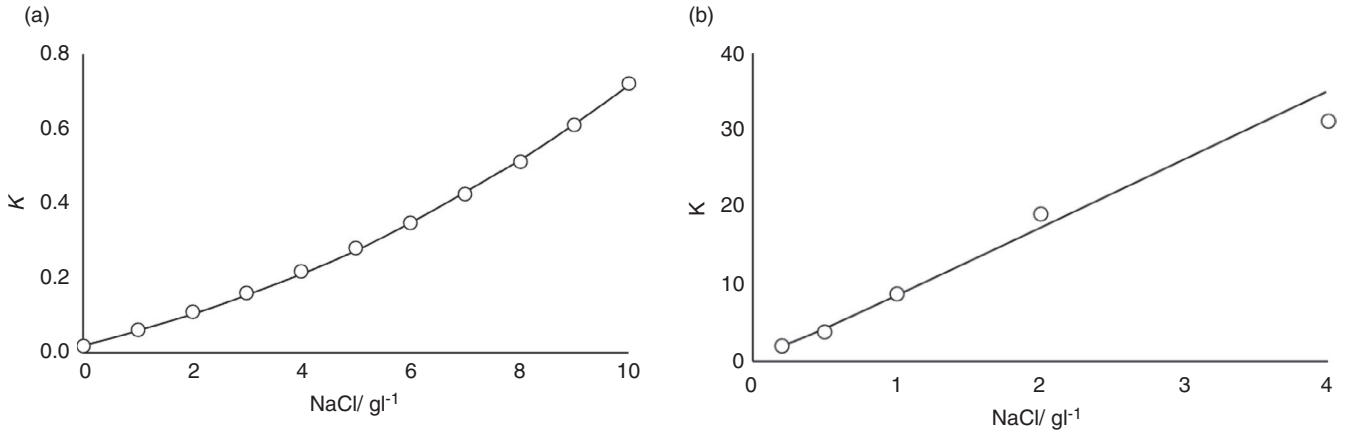

FIGURE 23 (A) Variation of K for a fictitious direct dye/NaCl/cellulosic fibre system as a function of the amount of added inorganic electrolyte present in the dyebath; plotted using data in Table 4, $[d_{int}]$ calculated using Equation 4 and K using Equation 8; (B) variation of K for C.I Yellow 12/NaCl/CV system at 40°C as a function of the amount of added NaCl present in the dyebath; K calculated using Equation 5 using data from[24]

high solubility in the dyebath phase, since it follows that in the absence of added inorganic electrolyte, values of $[d_{sol}]$ will be very high and, also, much greater than those of $[d_{disp}]$: thus, dye uptake will be very low in the absence of added NaCl or Na_2SO_4. Hence, the characteristically low substantivity displayed by direct dyes towards cotton and other types of cellulosic fibre in the absence of added NaCl or Na_2SO_4 is a corollary of the dye's marked inclination to favour the aqueous dyebath phase, $[d_{sol}]$, rather than the interstitial fibre phase, $[d_{int}]$, because of the dye's inherent high solubility.

In contrast, when dyeing is carried out in the presence of added inorganic electrolyte, the solubility of the direct dye is reduced and dye aggregation encouraged, so that values of $[d_{sol}]$ will be low, with those of $[d_{disp}]$ being much higher than those of $[d_{sol}]$. In such a case, dye uptake is therefore promoted because the solubility of the direct dye in the dyebath phase, $[d_{sol}]$, has been reduced. The interstitial models of dyeing therefore predict that in the presence of added NaCl or Na_2SO_4, the innate preference of the formerly highly soluble direct dye to prefer the aqueous dyebath phase shifts towards the interstitial fibre phase, $[d_{int}]$, because the solubility of the dye in the dyebath phase, $[d_{sol}]$, has been reduced.

A simple explanation is therefore provided for the promotional effect imparted by added inorganic electrolyte to direct dye uptake on cotton. Added NaCl or Na_2SO_4 reduces the solubility of the dye in the dyebath which increases the intrinsic disposition of the large size, planar dye molecules to aggregate, thereby shifting the innate preference of the formerly highly soluble direct dye to prefer the aqueous phase in favour of the fibre phase, which thus promotes dye-fibre substantivity and increases dye uptake. The effect of added inorganic electrolyte on direct dye solubility described by Equation 8 therefore supports the proposal[44] that the use of NaCl or Na_2SO_4 in the exhaust application of direct dyes to cotton (and other types of cellulosic fibre) facilitates the controlled transfer of the dye from the aqueous dyebath phase to the fibre phase.

7 | MECHANISTIC MODEL OF DIRECT DYE ADSORPTION

According to the notion[205] recounted above, that the solubility of a direct dye molecule in an aqueous dyebath is the primary contributor towards dye-fibre substantivity, as articulated via the concept of interstitial water applied to both direct dyes and reactive dyes on cotton data,[205,209] the manner by which the dyes are adsorbed on cellulosic fibres in the absence of added NaCl or Na_2SO_4 can be represented by a simple model [see [205] for a detailed account], which considers the effects of added inorganic electrolyte on the physical state of the direct dye present in the dyebath phase and the fibre phase during the course of a typical dyeing process.

7.1 | Dyebath phase

In the initial stages of dyeing cotton using direct dyes, which is commonly undertaken at low temperature, the dyebath phase will contain monomolecularly dissolved dye anions. In addition, because of the innate tendency of the large, planar direct dye molecules to self-associate via coplanar association, dye aggregates will also be present in the low temperature aqueous dyebath. These dimeric, trimeric, etc. direct dye aggregates will comprise dye molecules that possess lower aqueous solubility than their monomolecular dye counterparts. Owing to their inherent low solubility, the dye aggregates will likely coalesce, resulting in the formation of

very low solubility dye particles that comprise clusters of dye aggregates which, in turn, contain numerous low solubility, self-associated dye molecules.

According to the concept of interstitial water in dyeing as applied to the direct dye/cellulosic fibre system,[205] an aqueous direct dye dyebath in the initial stages of dyeing will therefore comprise three different types of dye species namely:

1. high solubility monomolecular dye anions;
2. low solubility dye aggregates that comprise several dye molecules of reduced solubility;
3. dye particles of very low solubility that comprise clusters of low solubility dye aggregates.

The dissolved monomolecular direct dye anions will be present in the form of a bulk dyebath dye solution, d_{sol}, and the direct dye aggregates and dye particles will be present in the form of a *bulk dyebath dye dispersion*, d_{disp}. The relative amounts of each of the three different types of dye anions/aggregates/particles that reside within a given aqueous dyebath phase will vary depending on the particular dyebath conditions encountered, namely the dye concentration, liquor ratio, temperature and, of course, the amount of added inorganic electrolyte.

This is because high dye concentrations, low liquor ratios (which are analogous to high dye concentrations) and low dyebath temperatures, which commonly are encountered in the initial stages of direct dye application, are each known to encourage dye self-association; in contrast, higher temperatures, low dye concentrations and longer liquor ratios are well-known to disfavour dye aggregation.

Accordingly, the aqueous dyebath dye dispersion phase can be assumed to predominate in the early stages of dyeing because of the inherent propensity of the dye molecules to undergo self-association, especially at low temperatures in the presence of added inorganic electrolyte, so that $d_{sol} <<< d_{disp}$ (Figure 24).

However, as dyeing proceeds and dyebath temperatures increases, the extent of dye self-association will decrease, owing to the endothermic nature of dye aggregation, and the aggregates will therefore break down, releasing monomolecular dye anions which will dissolve in, and therefore enlarge, the aqueous dyebath dye solution phase, d_{sol}. As temperature increases further, dye particles that are present the bulk dyebath dye dispersion will gradually liberate dye aggregates, which in turn, will break down and furnish additional monomolecular dye molecules that dissolve in, and thereby, further augment the bulk dyebath dye solution, d_{sol}. Consequently, as dyebath temperatures increases, the magnitude of the aqueous dyebath dye dispersion, d_{disp}, decreases, whilst that of the aqueous dyebath dye solution, d_{sol}, increases, correspondingly (Figure 24).

As the maximum dyeing temperature of, say 98°C, is reached, the aqueous dyebath phase will be dominated by the presence of dissolved, highly mobile, monomolecular dye anions which are able to transfer from the bulk dyebath dye solution, d_{sol}, to the interstitial dye solution, d_{int}, that resides within the amorphous domains of the fibre phase, wherein they diffuse, interact with appropriate sites/regions in the composite cellulose polymer chains and, eventually, become adsorbed. The depleted interstitial dye solution, d_{int}, will then be replenished by the transfer of dissolved direct dye anions from the bulk dyebath dye solution, d_{sol}, thereby enabling further dye diffusion/interaction/adsorption to occur within the substrate. In turn, the bulk dyebath dye solution, d_{sol}, will be replenished by the release of monomolecular dye anions from the dye aggregates present in the bulk dyebath dye dispersion, d_{disp}; dye particles present in the bulk dyebath dye dispersion, d_{disp}, will liberate dye aggregates, which, in turn, are then able to furnish additional monomolecular dye molecules which can dissolve in, and, thereby, replenish the bulk dyebath dye solution, d_{sol}, from which dissolved dye anions can transfer to the interstitial dye solution, d_{int}, and further dye adsorption can occur.

The interstitial dye solution therefore acts as a conduit for the transfer of the direct dye molecules from the dyebath phase to the fibre phase. The sequential process of the transfer of direct dye molecules from the bulk dyebath dye dispersion, d_{disp}, to the bulk dye solution, d_{sol}, to the interstitial dye solution, d_{int}, continues until all of the direct dye has been adsorbed or the cotton is saturated with adsorbed dye.

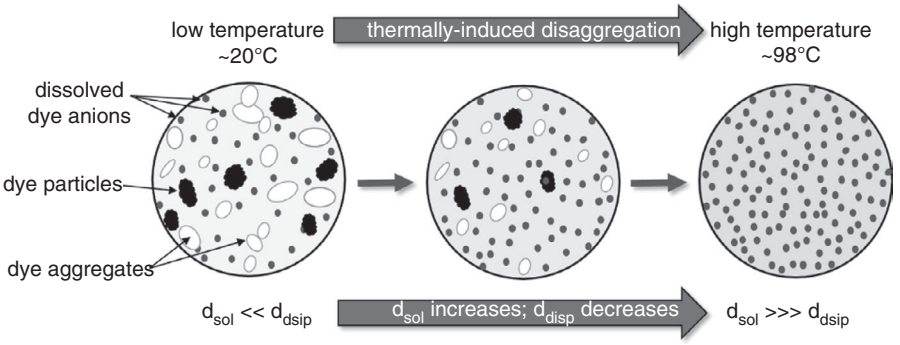

FIGURE 24 Representation of direct dye/cotton adsorption mechanism: dyebath phase

7.2 | Fibre phase

From the viewpoint of the nature of the direct dye molecules within the fibre phase, during the high temperature stages of dyeing (~98°C), the cellulosic fibre will contain predominantly dissolved, monomolecular dye anions, as $d_{sol} >>> d_{disp}$ (Figure 25).

During the subsequent cooling stage of the dyeing process, the solubility of the dyes will decrease and dye self-association within the cotton fibre will increase, owing to the intrinsic amphiphilic nature of the large molecular size dye molecules and the endothermic nature of the dye aggregation process: the presence of inorganic electrolyte within the dyed substrate can also be expected to encourage dye self-association in-situ within the fibre. This will result in the formation of low solubility direct dye aggregates as well as very low solubility dye particles in situ within the dyed substrate (Figure 25). Consequently, at low temperature, the interstitial phase of the (dyed) fibre will comprise a high proportion of dye aggregates and dye particles, because of the inherent propensity of the dye molecules to undergo self-association, especially at low temperatures in the presence of added inorganic electrolyte, so that $d_{sol} << d_{disp}$, though individual dye molecules are likely also present (Figure 25).

7.3 | Thermally-driven dye aggregation/disaggregation

The above model of the direct dye/inorganic electrolyte/cotton system as depicted from the state of the direct dye molecules in both the dyebath phase (Figure 24) and fibre phase (Figure 25), implies that the aqueous dyeing of cellulosic fibres using direct dyes in the presence of added inorganic electrolyte is, in effect, a *thermally-driven, aggregation/disaggregation process*, as represented by Figure 26.

Under the low temperature conditions encountered at the start of dyeing, the presence of the added NaCl or Na_2SO_4 reduces the solubility of the dye/dye precursor anion in the aqueous dyebath phase to a low level that encourages dye aggregation and the formation of dye particles, which results in dye-fibre substantivity being very low. However, as dyebath temperature is increased, the greater thermal energy exploits the endothermic nature of the dye aggregation process, so that dye dis-aggregation is encouraged and, also, dye solubility increases, with the result that at high dyeing temperatures, high solubility, monomolecular dye anions predominate which display substantivity towards the cellulosic substrate. During the later stages of dyeing, when the dyed fibre is cooled, the lower thermal energy once again exploits the endothermic nature of the dye aggregation process so that dye aggregation is encouraged and, also, dye solubility decreases, with the result that low solubility dye aggregates/particles are formed in situ within the fibre.

In essence, the role of added inorganic electrolyte in the direct dye/inorganic electrolyte/cotton system is to reduce the solubility of the direct dye molecules in the dyebath to such an extent that dye-fibre substantivity, and thereby dye uptake, can be controlled via dyebath temperature regulation. At low temperatures, the combined effects of electrolyte-induced reduced dye solubility and increased dye self-association simply convert the original highly soluble/low substantivity direct dye molecules into the corresponding low-solubility/low substantivity aggregated form in the dyebath, from which high solubility, monomolecular dye anions can be subsequently liberated during dyeing in a controlled and convenient manner by the thermally-regulated dye dissolution process depicted in Figure 27.

At high dyeing temperatures, the presence of added inorganic electrolyte in the dyebath ensures that the solubility of the liberated monomolecular dye anions is nevertheless at a particular reduced level which reverses the innate predisposition of the direct dye anions to favour the dyebath phase rather than the fibre phase and, therefore, dye uptake is promoted.

In effect, the combined effects of electrolyte-induced reduced solubility and increased dye self-association result in the dye being able to be transferred, in a controlled, thermally-regulated manner, from the aqueous dyebath onto the fibre (Figure 28).

Thus, Figure 28 concurs with the previously recounted notion[205] that the solubility of the direct dye in the aqueous dyebath is the principal contributor towards dye-fibre substantivity and, thereby, is the main determinant of dye uptake, as expressed in terms of the concept of interstitial water in dyeing.

The fact that the above dye adsorption model predicts that the adsorbed direct dye molecules will be present in the fibre phase at the end of dyeing predominantly as dye aggregates/particles explains why direct dyes on cotton and other types of cellulosic fibre display characteristically only low/moderate levels of fastness to wet treatments (e.g. domestic laundering) which can be improved, markedly, by recourse to an aftertreatment,[22,139,240-243] most popularly in the guise of *cationic fixing agents*. Even though the adsorbed dye molecules may be present in the dyed substrate, for the most part, in the form of low solubility dye aggregates/particles, as these species are retained only physically within the dyed fibre, they will nonetheless display a marked inclination to diffuse out of the dyed material during especially warm/hot wet treatments, such as laundering, and therefore display only low/moderate levels of wet fastness.

An implicit assumption is made in the above model of dyeing using direct dyes in the presence of added NaCl, which was considered to also apply in the case of the dyeing of cotton using reactive dyes,[209] namely, that only

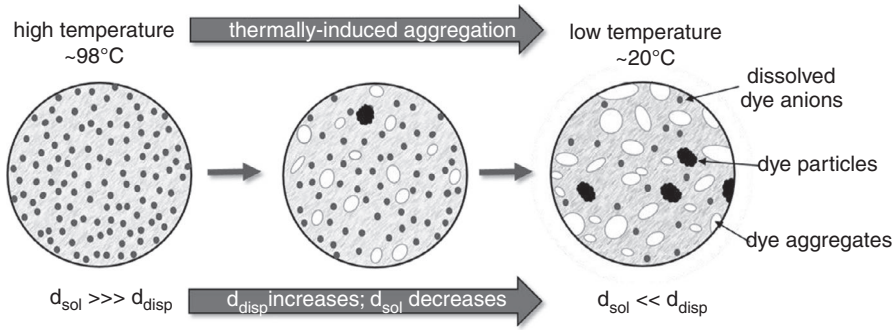

FIGURE 25 Representation of direct dye/cotton adsorption mechanism: fibre phase

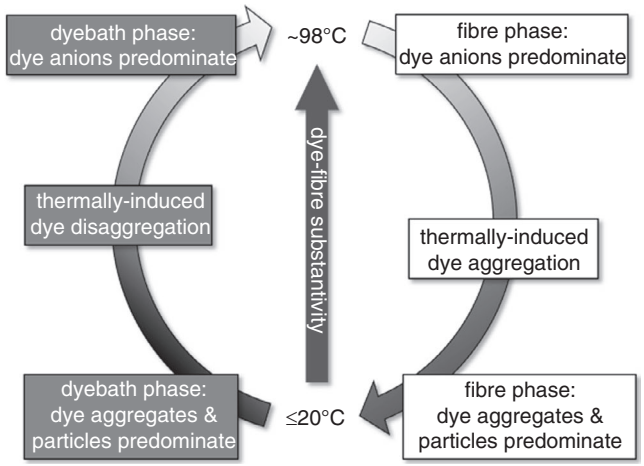

FIGURE 26 Thermally driven, aggregation/disaggregation mechanism of direct dye adsorption

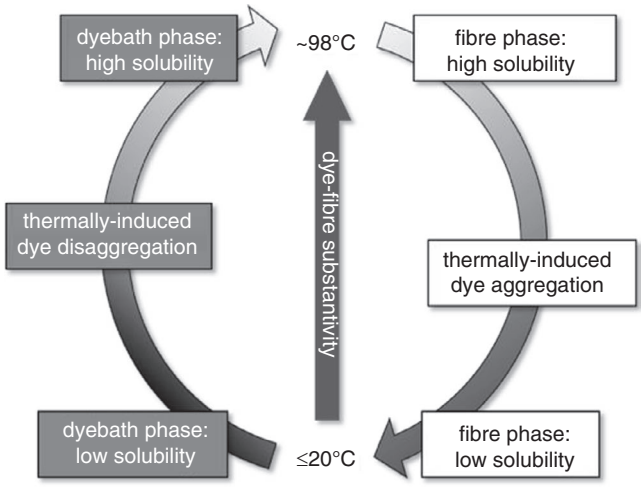

FIGURE 27 Thermally driven dye solubility mechanism of direct dye adsorption

disaggregated, monomolecular dye anions transfer from the dyebath phase to the interstitial regions of the fibre phase, interact with appropriate groups/sites within the cellulose macromolecule and become adsorbed: this assumption merits its examination.

As mentioned, whilst the precise nature of the physical state of all classes/types of dye molecule in both the aqueous dyebath phase and fibre phase during an exhaust dyeing process, has not been unequivocally established, as most classes of dye display a conspicuous proclivity to self-associate in aqueous solution, it is commonly viewed that dye aggregation is a common feature of all exhaust dyeing processes. Unfortunately, the relative paucity of unambiguous experimental evidence obtained during immersion dyeing processes neither supports nor refutes the notions that dye molecules are present in monomolecular form or in particulate form in the dyebath phase. For example, whilst direct dye adsorption was considered to likely proceed in the form of dimers at 60°C in the presence of added electrolyte,[216] some workers feel that owing to thermally induced disaggregation effects, direct dyes display negligible aggregation under typical immersion dyeing conditions,[244] though electrolyte-induced aggregation has been observed to occur even at 90°C.[194] A similar, but even more ambiguous situation applies in the case of attempts to elucidate the physical state of dye molecules in the fibre phase during exhaust dyeing processes, owing to the considerably greater experimental challenges that such studies involve.

Whilst the interstitial model of dyeing assumes that monomolecular direct dye molecules are adsorbed by cotton, the model could be adapted to include the adsorption of both monomolecular dye anions as well as that of direct dye aggregates and even dye particles. As to how, experimentally, such a revised model of direct dyeing might be confirmed or repudiated, is not straightforward; how a revised model might furnish additional clarification of the promotional effect of added inorganic electrolyte on direct dye uptake, is unclear.

7.4 | Applicability to other anionic dye/dye precursors

According to the above interstitial model of direct dye adsorption, the characteristic low substantivity displayed by direct dyes towards cotton when applied in the absence of added NaCl or Na_2SO_4 can be attributed to the dyes' high aqueous solubility and corresponding pronounced inclination

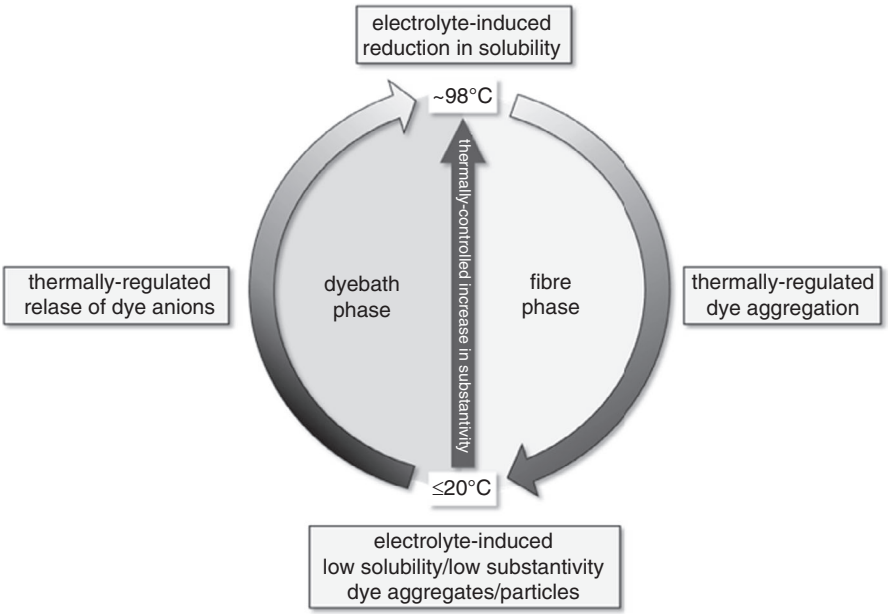

FIGURE 28 Thermally driven dye transfer mechanism of direct dye adsorption

to remain in the aqueous dyebath phase rather than to transfer to the fibre phase. The addition of NaCl or Na_2SO_4 to the direct dye or reactive dye dyebath therefore reduces the solubility of the dyes with the result that the intrinsic preference of the formerly high solubility direct dye or reactive dye to favour the aqueous dyebath phase swings towards the fibre phase and, thereby, dye uptake is promoted.

This particular theoretical mechanism was subsequently confirmed in a series of practical studies of the promotional effect of NaCl on the uptake of direct dyes,[25] commercial grade reactive dyes[26] and purified reactive dyes[231] on cotton.

It therefore seems reasonable to suggest that an identical mechanism can be assumed to apply in the cases of the phenolate, Ar-O^-, enolate, -C-O^- and thiolate -S^-, derivatives of azoic coupling components, vat dyes and sulphur dyes, respectively, which also display characteristically low substantivity towards cotton in the absence of added NaCl or Na_2SO_4. It can then be proffered that added inorganic electrolyte reduces the dye/dye precursor's high aqueous solubility, thereby inverting the inherent proclivity of the various types of dye/dye precursor anion to favour the aqueous dyebath phase rather than the fibre phase.

In terms of the exhaust application of azoic coupling components, vat dyes, sulphur dyes, reactive dyes and direct dyes to cotton in the presence of added inorganic electrolyte, as the (conceptually and experimentally unconvincing) 'neutralising' effect which added inorganic electrolyte apparently exerts upon the negative charge developed at the cotton fibre surface can be assumed to be more or less the same, irrespective of the type of dye/dye precursor involved, it seems reasonable to suggest that the principal reason why a specific amount of added NaCl or Na_2SO_4 is required for dyeing, as exemplified by the data shown in Figure 11, is to reduce the solubility of the respective anionic derivative (i.e. Ar-O^-, Dye-S^-, Dye-C-O^- and Dye-SO_3^-) within the dyebath phase to a particular extent that is necessary to promote dye-fibre substantivity to a given level required for the given type of dye/dye precursor under the particular dyeing conditions employed. As such, it can be expected that the amount of added inorganic electrolyte, as illustrated by Figure 11, will therefore necessarily vary according to the solubility of the given type of dye/dye precursor under the particular dyeing conditions (pH, temperature, liquor ratio, etc.) in operation.

As such, the well-known variation in the amount of added inorganic electrolyte required for applying direct dyes, vat dyes, reactive dyes, etc., to cotton, as illustrated by the values shown in Figure 11 and Table 1, reflect the relative solubility of the particular type of dye/dye precursor anion under the particular dyebath conditions in operation: the higher the solubility of the enolate, thiolate, etc., the greater is the amount of inorganic electrolyte that must be added to the dyebath. Though typical values of the solubility of the thiolate, enolate and phenolate forms of sulphur dyes, vat dyes and azoic coupling components, respectively, are not commonly available, it seems reasonable to suggest from Figure 11 that relative dye/dye precursor anion solubility, under the typical dyebath conditions utilised, likely follows the order:

direct dyes < sulphur dyes < azoic coupling components < vat dyes < < < reactive dyes

The linkage between the solubility of a dye/dye precursor anion in the dyebath phase and the level of substantivity displayed by the particular dye/dye precursor towards cotton or other type of cellulosic fibre can be illustrated by recourse

to vat dyes. Essentially, vat dyes are commonly classified by dye makers according to their substantivity and the quantities of alkali, reducing agent and, of relevance to this paper, added inorganic electrolyte, that is required for their immersion application to cotton or other type of cellulosic fibre. Whereas NaCl or Na_2SO_4 is employed to promote uptake of high solubility, low substantivity vat dyes at low temperatures (e.g. 20-30°C), inorganic electrolyte is not employed in the cases of lower solubility, high substantivity vat dyes that are typically applied at 60°C. This shows that inorganic electrolyte is therefore employed for low substantivity enolate (-C-O$^-$) derivatives in order to counteract their inherent high aqueous solubility, by encouraging aggregation within the dyebath, which reduces the solubility of the enolate vat dye derivative under the strongly alkaline dyebath conditions and thereby increases dye-fibre substantivity, resulting in enhanced dye uptake.

8 | THE PROMOTIONAL EFFECT OF REDUCED LIQUOR RATIO ON DYE UPTAKE DURING EXHAUST DYEING

As discussed in the first part of the paper,[1] the liquor ratio selected for dyeing influences several aspects of all exhaust dyeing processes (e.g. dye migration, dye levelling, dye solubility, etc.) primarily because liquor ratio determines the volume of the aqueous dyebath. From the perspective of this paper, it is well-known that reducing the liquor ratio utilised in the exhaust dyeing of cellulosic fibres exerts a promotional effect on the uptake of both direct dyes[245-248] and reactive dyes.[249-252]

To account for this phenomenon, models were proposed,[209,230] based on the concept of interstitial water in dyeing, according to which, lowering the liquor ratio used to apply direct dyes and reactive dyes to cotton, in both the absence and presence of added inorganic electrolyte, reduces the solubility of the dyes and encourages the inherent tendency of the planar, large molecular size, anionic dyes to aggregate in the aqueous dyebath, so that their intrinsic predilection to favour the aqueous dyebath phase shifts towards the fibre phase and dye uptake is thereby promoted.[209,230]

In essence, the hypotheses expressed in terms of Equation 8 applies,[209,230] insofar as, reducing the liquor ratio used for dyeing increases the amount of low solubility dye species,[d_{disp}], which therefore reduces the amount dye in solution within the dyebath phase, [d_{sol}], with the result that dye uptake, as expressed by [d_{int}], is promoted. Equation 8 therefore predicts that as liquor ratio decreases, the intrinsic preference of the hitherto high solubility direct dye or reactive dye to favour the aqueous phase moves towards the fibre phase.

As this particular mechanism is identical to that proposed to account for the promotional effect of added NaCl or Na_2SO_4 on the uptake of both direct dyes and reactive dyes on cotton,[205,209] it was concluded that lowering the liquor ratio used for dyeing and adding inorganic electrolyte to the dyebath exert the same promotional effect upon both direct dye and reactive dye uptake.[209,230]

This particular hypothesis was indeed confirmed by the findings of experimental studies of the uptake of both direct dyes and reactive dyes on cotton [25,26,231] insofar as the colour strength of 2% omf dyeings undertaken in the absence of added NaCl at low liquor ratios namely 1:2 and 1:1.5,[26,231] as well as 1:2, 1:1.5 and 1:1,[25,26,231] were of similar magnitude to those secured for dyeings which had been produced using 1:10, 1:20 and 1:50 liquor ratios in the presence of 20 g l^{-1} added NaCl in the case of direct dyes[25] and 50 g l^{-1} added NaCl in the case of reactive dyes.[26,231]

Because it is well-known that liquor ratio exerts marked promotional effects on the uptake of azoic coupling components, vat dyes and sulphur dyes on various types of cellulosic fibre,[253-256] it seems likely that the model proposed to account for the promotional effect imparted by reduced liquor ratio on the uptake of both direct dyes and reactive dyes on cotton,[209,230] can also be applied to azoic coupling components, vat dyes and sulphur dyes.

9 | CONCLUSIONS

Various theories/hypotheses/concepts have been proposed over many decades to explain the remarkable promotional effect which added inorganic electrolyte imparts to the uptake of vat dyes, sulphur dyes, azoic colorants, direct dyes and reactive dyes on cellulosic fibres.

Although the above analysis of these various theories suggests that suppressed dye-fibre electrical repulsion, electrolyte-induced increased water sorption and increased fibre specific volume may make a small contribution to the overall promotional impact of added NaCl or Na_2SO_4 on anionic dye/dye precursor uptake, the most likely explanation is that added NaCl or Na_2SO_4 reduces the solubility of the dye/dye precursor anion in the dyebath which increases the intrinsic disposition of the planar molecules to self-associate, which shifts the inherent preference of the formerly highly soluble dye/dye precursor anion from the aqueous phase to the fibre phase, thereby promoting dye-fibre substantivity and increasing dye/dye precursor uptake.

Such a situation is achieved by the combined effects of electrolyte-induced reduced solubility and increased dye self-association converting the highly soluble/low substantivity phenolate, Ar-O$^-$, enolate, -C-O$^-$, – SO_{3-}, etc. derivative into the corresponding low-solubility/low substantivity

aggregated form in the dyebath, from which high solubility, monomolecular dye/dye precursor anions can be liberated during dyeing by means of a thermally-regulated dissolution process depicted in Figure 27. As such water-dye/dye precursor solubility/aggregation effects are likely to be influenced by the effects which inorganic electrolyte ions exert upon the structure of water, it follows that electrolyte-water interactions may also contribute to the promotional impact of added NaCl or Na_2SO_4 on dye/dye precursor uptake.

The presence of added NaCl or Na_2SO_4 in the dyebath ensures that the liberated monomolecular dye/dye precursor anions display a suitably reduced level of solubility such that their intrinsic inclination to favour the aqueous dyebath phase shifts in favour of the fibre phase and dye uptake is thereby promoted. In essence, the role of added inorganic electrolyte in the dyeing of cellulosic fibres using azoic colorants, vat dyes, sulphur dyes, reactive dyes and direct dyes is to reduce the solubility and encourage the self-association of the respective dye/dye precursor anion in the dyebath to such an extent that the dye/dye precursor anion can be transferred, in a thermally-regulated, controlled manner from the aqueous dyebath onto the fibre (Figure 28).

According to this mechanism, which can be explained from a qualitative perspective by the simple expression presented in Equation 8, the manner by which added inorganic electrolyte promotes dye/dye precursor anion-cellulosic fibre substantivity and, therefore, enhances dye uptake, is dominated by the solubility of the dye in the dyebath phase.

The amount of added inorganic electrolyte required for dyeing will therefore depend upon the relative solubility of the particular anionic derivative (i.e. Ar-O^-, Dye-S^-, Dye-C-O^- and Dye-SO_3^-) under the particular dyebath conditions (pH, temperature, liquor ratio, etc.) in operation. Such a notion explains why specific amounts of added NaCl or Na_2SO_4 are employed for a given azoic coupling component, vat dye, direct dye, etc. (Figure 11), so as to reduce the solubility of the respective anionic dye/dye precursor species within the dyebath phase to that necessary to enable thermally-regulated dye transfer.

It is likely that the same dye transfer mechanism also accounts for the well-known promotional effect imparted by reduced liquor ratio on the uptake of the five classes of dye on cellulosic fibres.

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