



UNIVERSITY OF LEEDS

This is a repository copy of *The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres.*

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/121280/>

Version: Accepted Version

Article:

Burkinshaw, SM orcid.org/0000-0001-9940-1354 and Salihu, G (2019) The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres. *Dyes and Pigments*, 161. pp. 605-613. ISSN 0143-7208

<https://doi.org/10.1016/j.dyepig.2017.09.024>

© 2017 Elsevier Ltd. All rights reserved. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

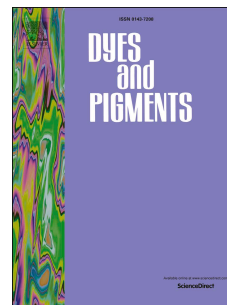


eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Accepted Manuscript

The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres

Stephen M. Burkinshaw, George Salihu



PII: S0143-7208(17)31777-1

DOI: [10.1016/j.dyepig.2017.09.024](https://doi.org/10.1016/j.dyepig.2017.09.024)

Reference: DYPI 6249

To appear in: *Dyes and Pigments*

Received Date: 18 August 2017

Revised Date: 11 September 2017

Accepted Date: 11 September 2017

Please cite this article as: Burkinshaw SM, Salihu G, The role of auxiliaries in the immersion dyeing of textile fibres: Part 7 theoretical models to describe the mechanism by which inorganic electrolytes promote reactive dye uptake on cellulosic fibres, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.09.024.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 **The role of auxiliaries in the immersion dyeing of textile fibres: Part 7**
2 **theoretical models to describe the mechanism by which inorganic**
3 **electrolytes promote reactive dye uptake on cellulosic fibres**

4
5 ***Stephen M Burkinshaw and George Salihu**

6 s.m.burkinshaw@leeds.ac.uk; g.salihu@leeds.ac.uk

7 University of Leeds, Leeds, LS2 9JT, UK

8 *corresponding author

9
10 **Abstract**

11 A model is proposed to explain the manner by which the uptake of reactive dyes on cellulosic fibres
12 is promoted by the addition of NaCl or Na₂SO₄ to the dyebath. The theoretical model invokes the
13 concept of interstitial water in dyeing and suggest that increased dye uptake occurs because the
14 added inorganic electrolyte promotes dye aggregation which reduces the solubility of the dye in the
15 dyebath, so that the inherent preference of the highly soluble dye to favour the aqueous phase shifts
16 towards the fibre phase. It is proposed that the same model can account for the promotion of direct
17 dye uptake imparted by the reduction in the liquor ratio utilised for dyeing. As such, added inorganic
18 electrolyte and reduced liquor ratio are considered to exert a combinatorial promotional effect on
19 reactive dye uptake.

20
21 **Highlights**

- 22 • the role of liquor ratio in reactive dye application is modelled
- 23 • interstitial water is used to show that low liquor ratio reduces dye solubility
- 24 • reducing liquor ratio promotes dye aggregation

25
26 **keyword**

27 keywords: dyeing cotton; dyeing auxiliaries; electrolyte; reactive dyes; salt-free dyeing

28

29 **1 Introduction**

30 Although several types of dyeing auxiliary are available that offer different kinds of assistance to
31 immersion dyeing processes, the manner by which many auxiliaries function is unclear (1). An
32 analysis (2) of published work relating to the role of the most important auxiliary utilised in the
33 exhaust dyeing of cellulosic fibres with direct dyes, namely inorganic electrolyte (NaCl or Na_2SO_4),
34 enabled a theoretical model to be devised (3), which invoked the concept of interstitial water, to
35 explain the role of added NaCl or Na_2SO_4 in the application of direct dyes. The promotional effect of
36 added inorganic electrolyte on direct dye uptake was considered to arise because of the combined
37 effects of induced dye aggregation and consequent reduced dye solubility on the effective dye
38 concentration gradient that exists between the amount of dye in the dyebath and the amount of dye
39 in the fibre; two equations were derived to interpret this theoretical model of direct dye adsorption
40 (3). The same theoretical model was also able to explain the promotional effect which reducing the
41 liquor ratio used for dyeing has upon the uptake of direct dyes on cellulosic fibres and two equations
42 were devised (4). The model was then employed to interpret the results obtained for a series of
43 dyeings on cotton which had been carried out using commercial grade direct dyes, employing
44 different liquor ratios in both the absence and presence of added NaCl (5). It was shown (5) that
45 because adding inorganic electrolyte to a direct dye dyebath and reducing the liquor ratio used for
46 dyeing achieve the same outcome, namely promotion of direct dye uptake, it is possible to dye
47 cotton to realistic depths of shade using direct dyes in the absence of added inorganic electrolyte
48 through the use of very low liquor ratios. In an attempt to clarify the manner by which added NaCl or
49 Na_2SO_4 influences reactive dye uptake on cellulosic substrates, the previous part of the paper (6)
50 presented an analysis of published research findings relating to the promotional impact of added
51 inorganic electrolyte on reactive dye uptake.

52

53 In this part of the paper, the findings from this analysis (6) are used to develop a theoretical model
54 which explains the promotional effect imparted by added inorganic electrolyte on reactive dye

55 uptake; it will be shown that the same model can also explain the promotional impact of reduced
56 liquor ratio on reactive dye uptake.

57

58 In the next part of the paper, experimental results obtained by applying commercial grade reactive
59 dyes to cotton will be interpreted using the theoretical model so as to explain why it is possible to
60 dye cotton (and other cellulosic fibres) using reactive dyes in the complete absence of added
61 electrolyte at low liquor ratio.

62

63 **2 reactive dyes and the use of added inorganic electrolyte**

64 The essential features of reactive dyes, from the viewpoints of their structure and application, were
65 discussed in the preceding part of the paper (6). Since their commercial introduction over 60 years
66 ago, global consumption of this dye class on cotton and other cellulosic fibres has enjoyed steady
67 growth with the result that reactive dyes nowadays account for ~ 55-60% of global dye consumption
68 for cellulosic fibres (2).

69

70 Essentially, reactive dyes bear a close structural resemblance to direct dyes in that both types of
71 dye are essentially long, planar, anionic molecules solubilised by one or more ionised sulfonate
72 groups. However, in the case of reactive dyes, attached to the constituent chromogen (eg azo, AQ,
73 etc.) is a reactive system that contains one or more electrophilic groups which enable the dyes to
74 form a covalent bond with nucleophilic hydroxyl groups in the cellulosic substrate. Because the
75 reactive dye is covalently attached to the cellulosic substrate, ensuing dyeings display
76 characteristically very high levels of fastness to wet treatments, such as domestic washing, this
77 being in sharp contrast to their direct dye counterparts, which characteristically exhibit only low to
78 moderate wet fastness properties on cellulosic fibres.

79

80 To expedite dye-fibre reaction, reactive dyes are applied to cotton and other types of cellulosic fibre
81 under aqueous alkaline (eg NaOH, Na₂CO₃) conditions so that the cellulosic hydroxyl groups (ie
82 Cell-OH) are deprotonated, forming the far more strongly nucleophilic, ionised hydroxyl groups

83 (Cell-O⁻; aka *cellulosate anions*) within the substrate. Unfortunately, the alkali-induced generation of
84 the strongly nucleophilic, ionised hydroxyl groups within the substrate not only favour covalent bond
85 formation with the fibre but also promote undesirable alkali-induced hydrolysis of the reactive dye,
86 which results in all commercial types of reactive dye displaying intrinsically low levels of dye-fibre
87 fixation efficiency, of the order 60-80%. Furthermore, because dye hydrolysis and dye-fibre fixation
88 occur simultaneously during immersion dyeing, and the presence of any unfixated dye in the final
89 dyeing will result in inferior wet fastness, reactive dyeings must be subjected to an additional wash-
90 off treatment to remove all traces of un-reacted and/or non-reactive dye from the dyed material.
91 Hence, the immersion dyeing of cellulosic fibres using reactive dyes is a two-stage process in which
92 the dye is firstly applied under aqueous alkaline conditions to promote dye-fibre fixation (the dyeing
93 stage) and the dyed material is then subjected to a thorough, aqueous treatment to remove all
94 unfixated dye (the wash-off stage).

95
96 Owing to the essential structural similarity of reactive dyes and direct dyes, the adsorption of
97 reactive dyes on cellulosic fibres is assumed to occur in a manner analogous to that of direct dyes
98 (7); furthermore, the mechanism by which added inorganic electrolyte promotes reactive dye uptake
99 prior to dye-fibre fixation is also assumed to be analogous to that described for direct dye uptake
100 (7). In order to secure satisfactory levels of dye uptake inorganic electrolyte, in the form of either
101 NaCl or Na₂SO₄, must be added to the aqueous dyebath in the cases of both direct dyes and
102 reactive dyes; in the case of reactive dyes, the added electrolyte also promotes the extent of
103 covalent fixation of the dye to the substrate (ie dye-fibre fixation). Indeed, the immersion application
104 of reactive dyes to cellulosic fibres is carried out typically in the presence of large amounts of
105 Na₂SO₄ or NaCl, with upto 100 g l⁻¹ in the case of dark shades. From the perspective of the size of
106 both the environmental and economic costs associated with the use of reactive dyes in cellulosic
107 fibre dyeing, it has been estimated (6) that in 2015, some 6,000,000 T of added inorganic electrolyte
108 may have been consumed in exhaust dyeing. Both the dyeing stage and subsequent wash-off stage
109 in reactive dyeing generate copious amounts of wastewater that contains residual hydrolysed dye,

110 unreacted dye, and very high levels of inorganic electrolyte, reactive dyeing wastewater typically
111 presents considerable environmental and economic challenge.

112

113 **3 proposed theory of the role of added electrolyte in the dyeing of cellulosic fibres using** 114 **reactive dyes**

115 As discussed (6), because the adsorption of reactive dyes onto cellulosic fibres in the absence of
116 dye-fibre reaction is assumed to parallel that of direct dyes, the mechanism by which the dyes are
117 adsorbed is also presumed to resemble that of direct dyes; consequently, the same theories which
118 have been proposed to explain the promotional effect imparted by added inorganic electrolyte on
119 the uptake of direct dyes are assumed to apply in the case of reactive dyes (6). Unfortunately, none
120 of these theories satisfactorily explains why reactive dyes (or direct dyes) display low uptake when
121 applied in the absence of added inorganic electrolyte nor can they account for the remarkable ability
122 of added NaCl and Na₂SO₄ to promote the uptake of reactive dyes on cellulosic substrates.

123

124 From an analysis of published research findings relating to the influence of added inorganic
125 electrolyte on reactive dye uptake, it was concluded (6) that the promotional effect imparted by
126 inorganic electrolyte can be attributed to the marked proclivity of the dyes to aggregate in aqueous
127 solution via coplanar association, a phenomenon that is encouraged not only by addition of
128 inorganic electrolyte but also high dye concentration. It was therefore considered (6) that adding
129 either NaCl or Na₂SO₄ to a reactive dye dyebath utilises the intrinsic propensity of reactive dyes to
130 self-associate in solution via coplanar association, which is a consequence of the dye's
131 characteristic long, planar structure and presence of one (or more usually) more sulfonate groups.
132 As such, the outstanding ability of inorganic electrolyte to promote reactive dye aggregation in
133 aqueous dyebaths can be attributed to the anionic charge on the dye anions derived from the -SO₃⁻
134 groups being shielded by the added electrolyte counterions (Na⁺), which reduces electrostatic
135 repulsion between neighbouring dye anions so that hydrophobic interaction between planar
136 aromatic rings in adjoining dye molecules are encouraged, which favours dye self-association. The
137 shielding effect of the added inorganic electrolyte Na⁺ counter-ions together with the strong π-π

138 interactions between aromatic centres in neighbouring dye molecules will result in the dye
139 molecules within the dye aggregates having lower aqueous solubility than their non-aggregated
140 direct dye counterparts that are present in solution within the dyebath. As the driving force for dye-
141 dye hydrophobic interaction is the need for the water molecules within the immediate proximity of
142 the reactive molecules to reduce their contact with the dye solutes, so that disruption of the
143 surrounding water structure by the dye molecules is minimised, the ensuing aggregates will
144 therefore tend to coalesce and form low solubility dye particles that will be present within the
145 dyebath in the form of a dispersion.

146

147 Hence, the addition of NaCl or Na₂SO₄ to an aqueous solution of a reactive dye reduces the
148 solubility of the dye, as has been observed (8, 9); since this reduction in dye solubility increases with
149 increasing amount of inorganic electrolyte (9, 10) the extent of electrolyte-induced dye aggregation
150 also increases with increasing amount of added NaCl or Na₂SO₄, as has also been observed (11). It
151 follows therefore that when sufficiently high amounts of added electrolyte are added to a reactive
152 dye solution, the resulting reduction in dye solubility is likely to be so pronounced as to result in dye
153 precipitation, especially when low liquor ratios are employed for dyeing, as again has been
154 observed and will be reported in the next part of the paper. It was therefore suggested (6) that
155 applying reactive dyes to cellulosic fibres in the presence of added inorganic electrolyte constitutes
156 a process of controlled dye precipitation onto the substrate, in which sufficient added electrolyte is
157 employed to induce the formation of a dispersion of dye particles in the aqueous dyebath without
158 imparting flocculation of the dye.

159

160 *3.1 the role of dye solubility in reactive dye uptake*

161 As previously recounted (6), reactive dyes display characteristically high aqueous solubility, as
162 exemplified by values of 70-100 gl⁻¹ @ 20°C (12), 60-120 gl⁻¹ at 25°C (13), 70 gl⁻¹ @ 20°C (14) and
163 50-100 gl⁻¹ @ 50°C (15). Because of this inherent high aqueous solubility, when a reactive dye is
164 dissolved in an aqueous dyebath that does not contain added inorganic electrolyte, the dye will
165 display an inherent predisposition to remain in the aqueous phase (ie the dyebath) rather than

166 transfer to the fibre phase; consequently, when applied in the absence of added NaCl or Na₂SO₄,
167 the extent of dye uptake onto the cellulosic substrate will be low. However, the above discussion
168 indicates that when inorganic electrolyte is added to a reactive dye dyebath, the solubility of the dye
169 is reduced (8-10) owing to enhanced dye self-association, which results in dye uptake onto the
170 cellulosic fibre being promoted. It therefore appears that the promotional effect of added NaCl or
171 Na₂SO₄ on reactive dye adsorption can be attributed to the intrinsic predisposition of the dye to
172 favour the aqueous phase having been markedly reduced, so that transfer of the dye to the
173 substrate is favoured and dye uptake therefore promoted. In essence, the characteristically high
174 aqueous solubility of reactive dyes, which is commonly conferred by the presence of sulfonate
175 groups in the dye molecules, is responsible for the inherently low substantivity displayed by the dyes
176 towards cellulosic fibres in the absence of added electrolyte; such high dye solubility is also the
177 reason why added inorganic electrolyte is so effective in promoting reactive dye uptake.

178

179 This particular argument was previously advanced to explain the promotional effect of added
180 inorganic electrolyte on the uptake of direct dyes on cellulosic fibres (3). That a similar rationale
181 might apply to both direct dyes and reactive dyes seems a reasonable proposition, when it is
182 recalled that the adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner
183 analogous to that of direct dyes and the mechanism by which added inorganic electrolyte promotes
184 reactive dye uptake prior to dye-fibre fixation is also assumed to be analogous to that described for
185 direct dye uptake (7).

186

187 In this context, it was proposed (3) that in the case of direct dyes, the solubility of the dye in the
188 dyebath is crucially important in terms of dye-fibre substantivity. By way of brief explanation, dye-
189 fibre substantivity reflects the attraction between a dye and a fibre that results from intrinsic physical
190 and chemical dye-fibre interactions that encourage the dye molecules to move from the aqueous
191 dyebath to the solid fibre. Such dye-fibre interactions are countered by dye-water interactions that
192 encourage the dye to remain within the aqueous dyebath and which resist dye-fibre substantivity.
193 Therefore, in essence, the extent of direct dye transfer from a dyebath to a cellulosic fibre depends

194 on the relative partition of the dye molecule between the aqueous dyebath (solution) phase and the
195 fibre (solid) phase, which, in turn, will depend upon the aqueous solubility of the dye. Furthermore, it
196 was proposed (3) that the solubility of a direct dye will also be a major contributory factor in the
197 process of dye diffusion whereby dye molecules spontaneously move from the dyebath phase to the
198 fibre phase as a result of the concentration gradient that exists between the two phases, since the
199 solubility of the dye will impact directly on the magnitude of the dye concentration gradient. Hence,
200 the most important aspect of an immersion dyeing process using direct dyes is the aqueous
201 solubility of the dye since it determines the tendency of the dye to favour either the dyebath phase
202 or the fibre phase and, thus, regulates the extent of dye transfer to the substrate.

203

204 An identical argument can be proposed in the case of reactive dyes since, as mentioned, they bear
205 a close structural resemblance to direct dyes and both the adsorption of reactive dyes on cellulosic
206 fibres and the mechanism by which added inorganic electrolyte promotes reactive dye uptake prior
207 to dye-fibre fixation, are assumed to be analogous to that described for direct dyes (7).

208

209 *3.2 a model to explain the adsorption of reactive dyes on cellulosic fibres*

210 Two approaches can be used to derive a model that explains reactive dye uptake on cellulosic
211 fibres in both the presence and absence of added inorganic electrolyte; as previously described in
212 the case of direct dyes and cellulosic fibres (3), such a model can also explain the promotional
213 effect of reduced liquor ratio on the immersion reactive dyeing system.

214

215 3.2.1 the theory of interstitial water

216 The concept of interstitial water has been described in terms of the development of a dyeing
217 processes (16) and wash-off processes (17-20) for various dye-fibre systems, as well as the
218 mechanism by which direct dyes are adsorbed onto cellulosic fibres (3). The concept is based on
219 the assumption that a very small proportion of the water that is employed in exhaust dyeing resides
220 within the interstices of the fibrous substrate. The amount of interstitial water within the substrate,

221 which corresponds to its moisture regain at 100% relative humidity (~ 0.22 l per kg^{-1} of fibre in the
222 case of cotton), is that required to saturate the textile substrate and impart the crucially important
223 actions of fibre wetting and fibre swelling. In the context of the model of dye adsorption described
224 below, the term interstitial water refers specifically to water which is adsorbed by the fibrous
225 substrate and, from which, the transfer of dye molecules/ions from the dyebath phase to the fibre
226 phase occurs (3). The remaining proportion of the water that is used in immersion dyeing processes
227 (~ 0.78 l kg^{-1} in the case of cotton) constitutes the bulk dyebath that surrounds the water-swollen
228 fibre phase and provides functions such as agitation, heating, dye dissolution, etc. As such, the
229 aqueous dyebath includes both interstitial water located within the swollen fibrous substrate as well
230 as bulk dyebath water located without the textile substrate. Thus, dissolved dye molecules will be
231 present within the interstitial dye solution in the fibre phase and, also, within the bulk dye solution in
232 the dyebath phase. The transfer of dye molecules from the bulk dye solution in the dyebath phase to
233 the solid fibre occurs via the interstitial dye solution within the fibre.

234

235 The concept of interstitial water in dyeing assumes (3) that in porous substrates, such as textile
236 fibres, different types of sorbed water are present namely:

- 237 • free water, which displays properties analogous to those of pure water in terms of
238 solvency and mobility;
- 239 • strongly bound water which is closely associated with the substrate and is immobile
240 and, therefore displays considerably different properties to those of free water;
- 241 • weakly bound water.

242 Such a model of water sorption compliments electric double-layer theory (13) which is commonly
243 utilised to describe the ionic environment within solutions of polar liquids, such as water, when they
244 are in the close vicinity of a charged surface, such as a textile fibre. Interstitial water is considered to
245 comprise the three types of sorbed water referred to above and, as such, according to the concept
246 of interstitial water in dyeing, the aqueous, ionic environment within the fibre interstices will be much
247 different to that within the surrounding bulk dyebath, owing to the presence of both immobile bound

248 water molecules and reduced mobility bound water molecules within the interstitial regions of the
 249 substrate, as well as the influence of the charged cellulosic fibre surface on the distribution of
 250 nearby sorbed ions/molecules (3). Therefore, the behaviour of dye molecules that are present within
 251 the interstitial water in the fibre differs to that of dye molecules that reside within the bulk aqueous
 252 dyebath that surrounds the fibre. A later part of the paper will provide a detailed account of
 253 interstitial theory of dyeing in the context of various dye-fibre systems.

254
 255 The wetted, swollen fibre therefore comprises an interstitial dye solution that is in intimate contact
 256 with dye solution that comprises the bulk dyebath which surrounds the fibre. It is considered that
 257 dyeing, or more correctly, the transfer of dye molecules from the aqueous phase (dyebath) to the
 258 fibre phase occurs from within this interstitial dye solution. Therefore, the aqueous dyebath
 259 comprises both interstitial water that resides within the swollen fibre as well as bulk dyebath water
 260 that is external to the textile substrate. Dissolved dye molecules are thus envisaged as being
 261 present within the interstitial dye solution in the fibre phase and within the bulk dye solution in the
 262 dyebath phase.

263
 264 In the case of the manner by which direct dyes are adsorbed on cellulosic fibres, such a situation
 265 was represented by Scheme 1, in which the aqueous dyebath comprises both an interstitial phase
 266 and a bulk dyebath phase (3). The transfer of dye molecules from the bulk dye solution in the
 267 dyebath phase to the solid fibre occurs via the interstitial dye solution within the fibre.

268

269

270

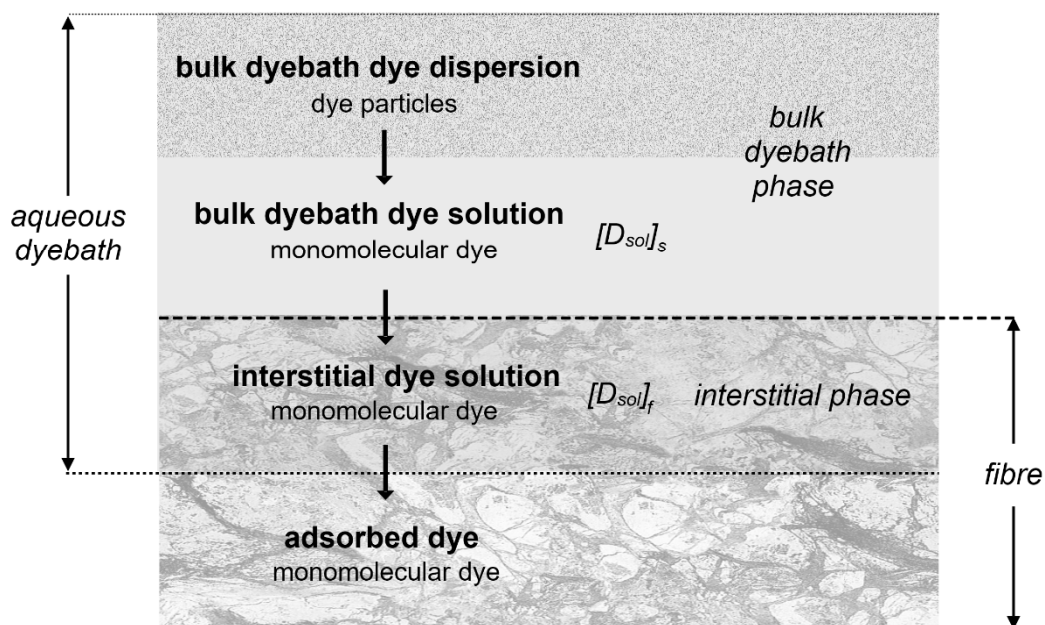
271

272

273

274

275



276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302

scheme 1 representation of direct dyeing mechanism (3)

Owing to the propensity of direct dye molecules to self-associate in solution, which is encouraged by the presence of added inorganic electrolyte, at the start of dyeing, a proportion of the dye will likely be present in the form of particles (ie aggregates of dye molecules) that will comprise a bulk dyebath dye dispersion within the bulk dyebath phase. Dissolved dye molecules/ions will also be present that make up a bulk dyebath dye solution; dissolved dye molecules will also populate the interstitial dye solution within the interstitial phase in the fibre. As dye aggregation decreases with increasing temperature, as dyeing proceeds, and the dyebath temperature increases, so the proportion of dye aggregates will reduce because dye molecules are released from the dye particles within the bulk dyebath dispersion and dissolve in the bulk dyebath solution; consequently, the proportion of dissolved dye ions within the dye solution in the dyebath will increase. Dye molecules that are present in the interstitial dye solution within the fibre will interact with the fibre and become adsorbed (for example, by means of a Freundlich-type or Langmuir-type process (2, 3)). As dye molecules are adsorbed onto the substrate, further dye molecules in the bulk dyebath solution transfer to, and replenish, the interstitial dye solution so that further dye adsorption can occur. Further dye molecules from the dye particles within the bulk dyebath dye dispersion are then released and dissolve in, and replenish, the bulk dyebath dye solution.

This process of dye dissolution from the bulk dyebath dye dispersion to the bulk dyebath dye solution, and the transfer of dye molecules/ions from the bulk dyebath dye solution to the interstitial dye solution, followed by dye molecule adsorption from the interstitial dye solution (as depicted by Scheme 1) continues until either all of the dye has been adsorbed or the fibre is saturated with dye.

303 Because of the close structural resemblance of reactive dyes to direct dyes (ie both dye types are
 304 characteristically, long, planar, anionic molecules solubilised by one or more ionised sulfonate
 305 groups) (6), coupled with the fact that prior to the reactive dye forming a covalent reaction with the
 306 cellulosic fibre, the adsorption of reactive dyes on cellulosic fibres is assumed to occur in a manner
 307 analogous to that of direct dyes, the mechanism by which added inorganic electrolyte promotes
 308 reactive dye uptake prior to dye-fibre fixation can be described in terms of the notion that dye
 309 adsorption proceeds from interstitial dye solution present within the substrate, as previously
 310 described for direct dye uptake (2, 3), displayed in Scheme 1.

311

312

313

314

315

316

317

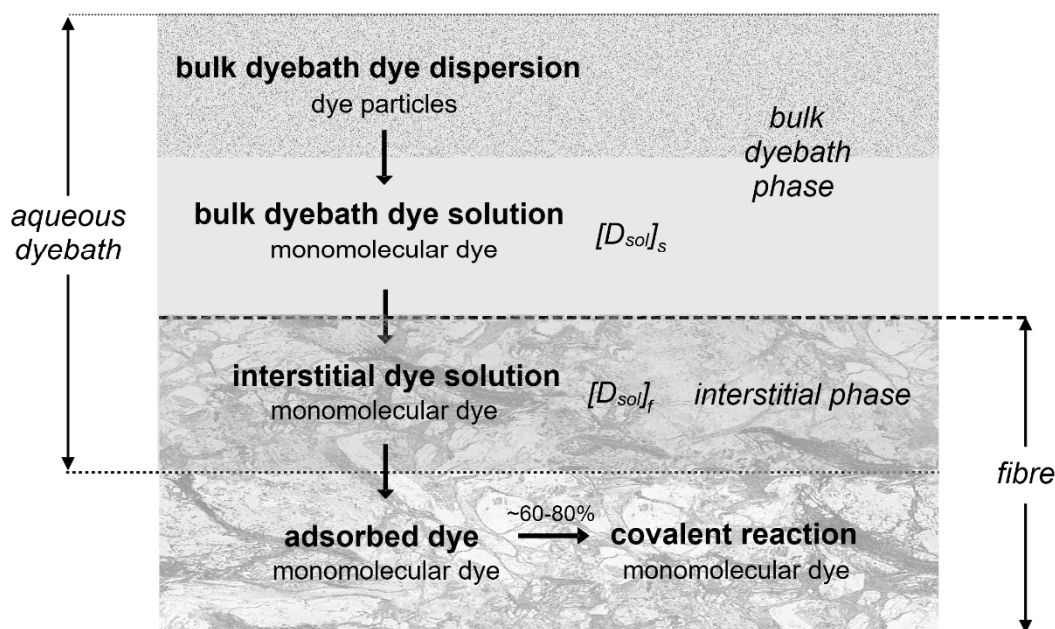
318

319

320

321

322



323

Scheme 2 representation of reactive dyeing mechanism

324

325 However, in the case of reactive dyes, as the adsorption of dye molecules onto the fibre from the
 326 interstitial dye solution can result in covalent bond formation with ionised hydroxyl groups in the
 327 substrate, Scheme 1 can be modified to include this (highly important) dye-fibre fixation stage of the
 328 dyeing process (Scheme 2). The inherent inefficiency of dye-fibre fixation displayed by reactive dyes
 329 on cellulosic fibres, which means that as much as ~30-50% of the dye applied can be present in the
 330 dyed substrate in the form of hydrolysed dye or unreacted dye, is reflected in Scheme 2.

331

332 3.2.2 the use of two equations to describe reactive dye adsorption

333 It was intended that the theoretical model of reactive dye adsorption depicted above should be
334 applicable to immersion dyeing processes in which dyeing had been carried out to equilibrium, as
335 well as dyeing processes in which equilibrium dye adsorption had not been achieved. To this end,
336 two approaches were employed to derive an equation which interpreted the above model of dye
337 adsorption namely:

338

- 339 i. one that describes the distribution of dye between the two phases at any point throughout
340 the immersion dyeing process;
- 341 ii. one that describes the effect of added NaCl or Na₂SO₄ on the distribution of the dye between
342 the fibre and dyebath phases at the end of an immersion dyeing process, irrespective of
343 whether or not equilibrium dye uptake had been achieved;

344

345 3.2.1.1 an equation that applies to dye uptake during immersion dyeing

346 To achieve complete dye exhaustion in immersion dyeing, the inherent tendency of dissolved
347 reactive dye molecules to move from the dyebath phase to the fibre phase under the influence of
348 the process of diffusion, that is driven by the dye concentration gradient between the dye in the
349 dyebath phase and the fibre phase, must be supplemented by dye-fibre substantivity. As mentioned
350 (6), the degree of substantivity displayed by a given reactive dye towards a particular cellulosic
351 textile fibre can be controlled by adjusting dyebath conditions (eg dyeing auxiliaries, controlling the
352 rate of temperature rise, etc.). As these adjustments principally regulate the solubility of the dye in
353 the aqueous dyebath, the primary contributor to reactive dye-cellulosic fibre substantivity and,
354 consequently, the predisposition of the dye to favour the fibre phase or dyebath phase, can be
355 assumed to be the solubility of the dye in the dyebath, as proposed in the case of direct dyes (3).
356 Hence, Eq 1, which was devised for direct dyes (3), can be used to relate dye-fibre substantivity to
357 dye solubility, in which $[D]$, the total amount of dye present within an immersion reactive dyeing

358 system comprises dye that is present in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$ as
 359 well as dye that is present within the bulk dyebath dye solution in the dyebath phase, $[D_{sol}]_s$. Eq 1
 360 was used to show that the intrinsic low substantivity displayed by direct dyes towards cellulosic
 361 fibres in the absence of added electrolyte is a consequence of the dye's high aqueous solubility and
 362 the ensuing preference of the dye to remain within the aqueous dyebath phase (3); a similar
 363 situation can be assumed to apply in the case of reactive dyes.

364

$$365 \quad S = \frac{[D_{sol}]_f}{[D_{sol}]_s} = \left(\frac{[D] - [D_{sol}]_s}{[D_{sol}]_s} \right) \quad 1$$

366

367 Since the ratio $[D_{sol}]_f/[D_{sol}]_s$ in Eq 1 describes the relative partition of the dye between the fibre phase
 368 and the solution phase; the higher the value of this ratio the greater is the distribution of the dye in
 369 favour of the fibre phase (ie $[D_{sol}]_f > [D_{sol}]_s$) and, therefore, the greater is the extent of dye uptake.
 370 The ratio $[D_{sol}]_f/[D_{sol}]_s$ therefore represents the degree of substantivity displayed by the reactive dye
 371 towards the cellulosic fibre at a given stage in the immersion dyeing process, and so S is the
 372 *substantivity coefficient* of the dye at a given point in the dyeing process.

373

374 Owing to the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$ in Eq 1, the degree of substantivity displayed by the dye
 375 towards the fibre, as reflected by the substantivity coefficient, S , will be determined by the amount of
 376 dye in the bulk dyebath dye solution, $[D_{sol}]_s$ relative to the total amount of dye within the dyeing
 377 system, $[D]$; the greater this difference, the higher will be dye-fibre substantivity, and, therefore, the
 378 greater the extent of dye uptake. Eq 1 therefore provides a model that relates both the degree of
 379 reactive dye-cellulosic fibre substantivity, via S , and the corresponding extent of dye uptake
 380 achieved, to the solubility of the dye: thus, Eq 1 provides an explanation for the nature of reactive
 381 dye-cellulosic fibre substantivity based on the role of dye solubility.

382

383 Since, according to the concept of interstitial water in dyeing, in Eq 1, the transfer of dye from the
 384 bulk dyebath dye solution, $[D_{sol}]_s$, to the interstitial dye solution, $[D_{sol}]_f$, as well as the total amount of

385 dye in the immersion dyeing system, $[D]$, are both expressed in terms of mass per unit volume (eg g
386 l^{-1}), because of the term $([D] - [D_{sol}]_f/[D_{sol}]_s)$, the substantivity coefficient S also has dimensions of
387 mass per unit volume (eg gl^{-1}). Such a situation seems reasonable when it is recalled that
388 substantivity coefficient, S , describes the tendency of the reactive dye to favour adsorption onto the
389 substrate and, according to the concept of interstitial water in dyeing, the adsorbed dye is assumed
390 to reside within the dye solution that is present in the interstitial phase within the fibre (ie $[D_{sol}]_f$).

391

392 Eq 1 predicts that the partition of the reactive dye between the fibre and dyebath phases during dye
393 adsorption depends on the concentration of the dye within the bulk dyebath solution phase, $[D_{sol}]_s$.

394 The addition of inorganic electrolyte to an aqueous reactive dye dyebath can therefore be
395 considered as a dilution effect, because the solubility of the dye is reduced as a result of electrolyte-
396 induced dye aggregation, which leads to a lower amount of dye in solution in the dyebath phase.

397 According to Eq 1, the driving force for the transfer of reactive dye molecules from the dyebath
398 phase to the fibre phase is expressed by the concentration gradient, $[D_{sol}]_f/[D_{sol}]_s$ that exists between
399 the amount of dye in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$, and the amount of dye
400 in the dye solution within the dyebath phase, $[D_{sol}]_s$. As dye solubility is reduced owing to dye
401 aggregation, it follows that in the presence of added NaCl or Na_2SO_4 , because $[D_{sol}]_s$ has been
402 lowered, the term $([D] - [D_{sol}]_f/[D_{sol}]_s)$ will increase and, therefore, the dye concentration gradient (ie
403 $[D_{sol}]_f/[D_{sol}]_s$) must also increase, so that a higher driving force for dyeing will be established.

404

405 As such, Eq 1 explains that the partition of the dye between the fibre and solution phases,
406 $[D_{sol}]_f/[D_{sol}]_s$ (ie S) increases in the presence of added NaCl or Na_2SO_4 because the amount of dye in
407 the dye solution within the bulk dyebath, $[D_{sol}]_s$, is lowered and, therefore, the amount of dye in the
408 interstitial dye solution within the fibre phase, $[D_{sol}]_f$, increases correspondingly. In effect, the
409 application of reactive dyes to cellulosic fibres in the presence of added inorganic electrolyte is
410 really a process of controlled precipitation of the dye within the fibre.

411

412 However, Eq 1 describes the likely partition of the dye between the interstitial dye solution within the
413 fibre phase and the bulk dye solution in the dyebath phase only in terms of the solubility of the dye.
414 It therefore does not take into account the involvement of other dyebath variables that can be
415 expected to participate in dye-fibre substantivity (eg temperature, dyebath-fibre interchange rate,
416 etc.). Thus, when using Eq 5, the value of the ratio $[D_{sol}]_f / [D_{sol}]_s$ is indicative only, insofar as, a low
417 value of $[D_{sol}]_f / [D_{sol}]_s$ implies that high dye solubility in the dyebath demotes dye uptake whereas a
418 high value of $[D_{sol}]_f / [D_{sol}]_s$ suggests that reduced dye solubility in the dyebath encourages dye
419 uptake.

420

421 The promotion of reactive dye uptake onto cellulosic fibres imparted by added inorganic electrolyte
422 can therefore be explained in terms of the model proposed for direct dyes on cellulosic fibres, (3),
423 namely, the combined effects of increased dye aggregation and reduced dye solubility on the
424 effective concentration of dye in the aqueous dye solution in the dyebath phase. Hence, the amount
425 of dye in the fibre solution phase (ie the fibre) is determined by the effect of the added inorganic
426 electrolyte on the concentration of reactive dye in the dyebath solution phase (ie the dyebath).

427

428 As discussed in section 4, this mechanism can also be used to describe the promotional effect of
429 reducing liquor ratio on the uptake of reactive dyes on cellulosic fibres in both the presence and
430 absence of added electrolyte.

431

432 3.2.1.2 an equation that applies to the final dye distribution at the end of dyeing

433 In terms of the mechanism by which reactive dyes are adsorbed on cellulosic fibres, Eq 2 is widely
434 accepted as describing the partition of dye between the fibre phase and the solution phase when
435 equilibrium dye uptake has been attained (ie when dye adsorption and dye desorption processes
436 are equal) (7). In Eq 2, $[D]_f$ is the amount of dye present in the fibre phase (ie the substrate) relative
437 to the amount of fibre and $[D]_s$ is the amount of dye in solution (ie the dyebath) relative to the
438 amount of solution. The distribution of the dye between the dyebath, s and fibre, f, phases is

439 described by the partition coefficient, K ; the higher the value of K the greater is the partition of the
440 dye in favour of the fibre phase (ie $[D]_f > [D]_s$) and the greater is dye uptake.

441

$$442 \quad K = \frac{[D]_f}{[D]_s} \quad 2$$

443

444 Equations based on Eq 2 are commonly used to calculate the thermodynamic standard affinity of
445 reactive dyes on cellulosic substrates, $-\Delta\mu^\theta$, taking into account the effect of alkali on the extent of
446 ionisation of the hydroxyl groups in the fibre (7). Eq 2 (and equations based upon it) therefore only
447 relates to the final distribution of dye between the fibre and dyebath phases (ie that achieved at the
448 end of an immersion dyeing process).

449

450 The analysis of equilibrium dye adsorption data using variants of Eq 2 is widely used as a means of
451 interpreting the mechanism by which reactive dye adsorption has occurred (in the absence of dye-
452 fibre reaction) in a manner analogous to that of direct dyes (7) and, therefore, is considered to
453 provide information about how reactive dye (and direct dye) molecules interact with the textile
454 substrate, for example, via specific site interactions (Langmuir-type) or non-specific site interactions
455 (Freundlich-type). However, the use of Eq 2 and variants to analyse isothermal equilibrium dye
456 adsorption data provides no information regarding the dyeing process prior to equilibrium, which,
457 from the viewpoint of a commercial immersion dyeing processes that are not carried out to
458 equilibrium, is a very important consideration. Also, equations such as Eq 2 (and others) are unable
459 to satisfactorily explain not only why reactive dyes display inherently low substantivity towards
460 cotton and other cellulosic fibres in the absence of added inorganic electrolyte but also why added
461 inorganic electrolyte (or reduced liquor ratio) so effectively promote dye uptake.

462

463 Eq 1 was therefore derived to address these issues in the case of direct dyes and cellulosic fibres
464 (3). In this context, whilst Eq 2 (and derivatives) offers information regarding the relative partition of

465 a dye between the fibre and dyebath phases at the end of dyeing, Eq 1 provides information about
466 how that partition may have been achieved.

467

468 It has been demonstrated (3) that, if dye solubility is assumed to be the major contributor to reactive
469 dye-fibre substantivity and, also, that the solubility of the reactive dye in the dyebath phase governs
470 the partition of the dye between the fibre and dyebath phases, the relationship represented by Eq 2
471 can be used to interpret the effect of electrolyte-induced aggregation and consequent reduced
472 solubility on the extent of direct dye at the end of an immersion dyeing process. Such a situation
473 applies in the case of dyeings which have not been carried out to equilibrium (3), since, in terms of
474 the work described in this part of the paper (and others that follow), the mechanism of reactive
475 dyeing from the viewpoint of dye-fibre interactions (prior to dye fixation), as normally revealed from
476 analysis of equilibrium dyeings using derivatives of Eq 2, is not sought. Instead, the aims of the work
477 undertaken were to firstly establish the motivational force that encourages the transfer of the
478 reactive dye molecules from the dyebath phase to the fibre phase and, secondly, to clarify the roles
479 of added inorganic electrolyte and reduced liquor ratio in this dye transfer process, under conditions
480 that mimic commercial dyeing (ie non-equilibrium) dyeing.

481

482 To this end, Eq 3 was derived (3) to explain the effect of added inorganic electrolyte on direct dye
483 adsorption, in which the total amount of dye within the reactive dyeing system, $[D]$, comprises dye
484 that is present in both the fibre phase, $[D]_f$ and the dyebath phase, $[D]_s$.

485

$$486 \quad K = \frac{[D]_f}{[D]_s} = \left(\frac{[D] - [D]_s}{[D]_s} \right) \quad 3$$

487

488 Therefore, the distribution of the reactive dye in solution between the fibre, $[D]_f$, and dyebath, $[D]_s$,
489 phases at the end of an immersion dyeing process is determined by the concentration of dye in
490 solution in the dyebath, $[D]_s$. The higher the value of this ratio (ie $[D]_f / [D]_s$) then the greater the
491 partition of the dye in favour of the fibre phase (ie $[D]_f > [D]_s$) and, therefore, the greater is the extent

492 of dye uptake onto the substrate. Eq 3 shows the marked dependency of final dye uptake (ie
493 $[D]_f/[D]_s$) and thus partition coefficient, K , on the solubility of the reactive dye in the dyebath, $[D]_s$.
494 The similarity between Eq 3 and Eq 1 is obvious.

495
496 According to Eq 3, when dyeing is undertaken in the presence of added Na_2SO_4 or NaCl , the
497 solubility of the reactive dye is reduced because of electrolyte-induced aggregation, so that the
498 effective concentration of dye in the dyebath (ie $[D]_s$) will be lowered. As the driving force for dyeing
499 (ie the transfer of dye molecules from the aqueous phase (dyebath) to the solid phase (fibre)), is the
500 concentration gradient, $[D]_f/[D]_s$, between the amount of dye in the dyebath, $[D]_s$, and fibre, $[D]_f$,
501 phases, then because the effective concentration of dye in the dyebath (ie $[D]_s$) is lowered in the
502 presence of added NaCl or Na_2SO_4 , then the term $([D] - [D]_s/[D]_s)$ will increase and, therefore, the
503 dye concentration gradient (ie $[D]_f/[D]_s$) will also increase, so that a higher driving force for dyeing is
504 developed.

505
506 Thus, Eq 3 predicts, as does Eq 1, that the amount of dye that is adsorbed by the substrate is
507 determined by the amount of dye in solution, which is depends upon the solubility of the dye in the
508 aqueous dye solution within the dyebath phase.

509

510 3.2.1.3 comparison of the two equations

511 Whilst Eq 1 and Eq 3 both describe the promotional effect imparted by added inorganic electrolyte
512 on reactive dye adsorption, the equations differ in terms of the nature of the data that is required for
513 their solution, because the two equations apply to different stage of the immersion dyeing process.
514 Eq 1 concerns the manner by which the reactive dye molecules transfer from the dyebath phase to
515 the fibre phase during the dye adsorption process (ie during dyeing), which therefore requires
516 information about the aqueous solubility of the dye in both the interstitial dye solution and the bulk
517 dyebath solution. Such data is not especially easy to collect: for example, in the case of non-
518 isothermal dyeing processes, the collection of data of this type would involve determining dye
519 solubility as a function of temperature and ionic environment, because dyebath temperature varies

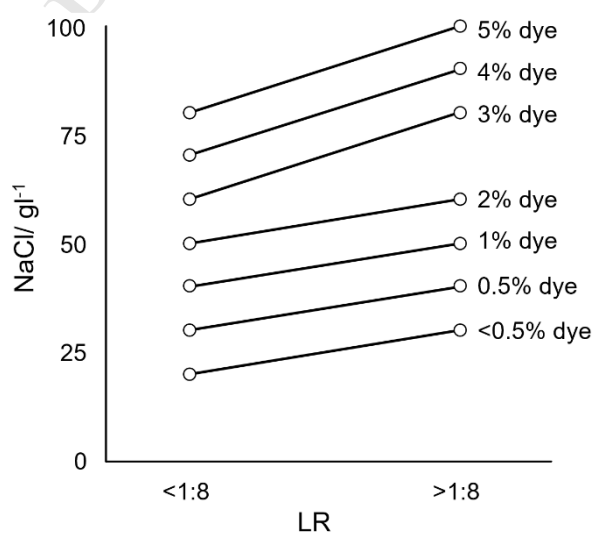
520 during dyeing and the dissociation of alkalis that are employed in reactive dyeing, such as NaHCO_3 ,
 521 varies as a function of temperature. Because Eq 3 describes how the particular final distribution of
 522 the reactive dye molecules between the dyebath and fibre phases was achieved at the end of the
 523 dye adsorption process (ie at the end of dyeing) for which knowledge of the far more easily
 524 experimentally measurable amounts of dye in the solid fibre and the dyebath at the end of dyeing
 525 are requires; thus Eq 3 offers a more amenable alternative to Eq 1.

526

527 **4 the role of liquor ratio in the dyeing of cellulosic fibres using reactive dyes**

528 The general effects of liquor ratio on immersion dyeing processes was discussed in the first part of
 529 the paper (1). In essence, the liquor ratio selected for reactive dyeing has a marked effect on the
 530 rate and extent of dye uptake as well as the degree of dye-fibre fixation achieved. Liquor ratio also
 531 influences the degree of substantivity displayed by the dye towards the fibre because the amount of
 532 water in the dyebath available for dye dissolution and, thus, the amount of dye available for
 533 adsorption, is determined by liquor ratio. Also, because the amount of dye used in dyeing is
 534 normally based on the mass of fibre (ie % omf), the effective dye concentration in the dyebath is
 535 also determined by liquor ratio. Hence, the intensity of the dye/inorganic electrolyte interactions that
 536 are responsible for promoting dye uptake are influenced greatly by liquor ratio.

537



538

539 Figure 1 effect of liquor ratio on amount of NaCl required for application of *Novacron FN* dyes; plotted using
540 data from (8)

541

542 Whilst the characteristically high aqueous solubility of reactive dyes is beneficial in terms of the
543 renowned ability of the dyes to respond in a controlled and predictable manner to added NaCl or
544 Na₂SO₄ during exhaust dyeing, the solubility of the dye in the aqueous dyebath, as reflected by the
545 liquor ratio used for dyeing, impacts directly on the effectiveness with which added electrolyte
546 promotes dye uptake. This is illustrated graphically by the data displayed in Figure 1 which shows
547 that the amount of added NaCl required for the application of *Novacron FN* (Huntsman) reactive
548 dyes increases with increase in liquor ratio as a function of the amount of dye applied (8). The
549 greater amounts of electrolyte required for dyeing when 3-5% omf dye is used at liquor ratios >1:8
550 are, presumably, to offset the comparatively higher levels of dye solubility at such long liquor ratios.

551

552 Several workers have sought to examine the effect of liquor ratio on reactive dye uptake [eg (21-24),
553 as exemplified by Gorenssek *et al* (25) who found that reducing liquor ratio increased both the extent
554 of dye uptake and fixation of four commercial monochlorotriazinyl reactive dyes on cotton, the
555 observed increase in uptake at lower liquor ratios being attributed to increased dye-fibre
556 substantivity (24). Whilst the promotional effect that a reduction in liquor ratio imparts to dye uptake
557 in immersion dyeing processes is a well-discussed topic, the precise nature by which this
558 promotional effect might be achieved has not been fully resolved.

559

560 4.1 proposed theory of the role of liquor ratio in the dyeing of cellulosic fibres using reactive dyes

561 Two approaches can be used to derive a model that explains why reducing the liquor ratio used for
562 dyeing increases the uptake of reactive dyes on cellulosic fibres, in both the presence and absence
563 of added inorganic electrolyte.

564

565 4.1.1 an equation that applies to dye uptake during immersion dyeing

566 Recourse can be made to the model that describes the effect of reducing liquor ratio on the
 567 adsorption of direct dyes on cotton, which invokes the concept of interstitial water in dyeing (4).
 568 When the liquor ratio used for dyeing is lowered, it follows that the solubility of the reactive dye will
 569 be lowered, because the amount of water available for dissolution of the dye has reduced. Thus, in
 570 terms of Eq 1, as the amount of reactive dye in solution in the dyebath phase, $[D_{sol}]_s$, has been
 571 reduced then the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$ will increase and, therefore, the dye concentration gradient
 572 (ie $[D_{sol}]_f/[D_{sol}]_s$) will also increase, so that a higher driving force for dyeing will be established.

573

574 In the case of direct dye adsorption (2), this effect was expressed by Eq 4, where L is the fractional
 575 liquor ratio given by Eq 5, in which m is the mass of fibre and v the volume of dyebath used in
 576 dyeing (the units of L are mass/volume, such as $g\ l^{-1}$); such a model can be used for reactive dyes.

577

578 As values of L will increase with decreasing liquor ratio (eg $L = 0.01$ in the case of a 1:100 liquor
 579 ratio; $L = 0.02$ for a liquor ratio of 1:50; $L = 0.1$ for a 1:10 liquor ratio, etc.), the marked dependency
 580 of final dye uptake (ie $[D_{sol}]_f/[D_{sol}]_s$) and thus partition coefficient, K , on dye solubility in the dyebath,
 581 $[D_{sol}]_s$ described by Eq 1 is directly impacted by liquor ratio via the term $[D_{sol}]_s/L$ in Eq 4 (3).

582

$$583 \quad K = \frac{[D_{sol}]_f}{\frac{[D_{sol}]_s}{L}} = \left(\frac{[D] - \frac{[D_{sol}]_s}{L}}{\frac{[D_{sol}]_s}{L}} \right) \quad 4$$

584

$$585 \quad L = \frac{m}{v} \quad 5$$

586

587 Although liquor ratio, via L , has a direct impact upon the amount of dye in solution in the bulk
 588 dyebath phase, $[D_{sol}]_s$, liquor ratio will also have an indirect influence upon the amount of dye in the
 589 interstitial solution in the fibre, $[D_{sol}]_f$, because of the term $([D_{sol}]_s/L)$, in that as values of $[D_{sol}]_s$
 590 decrease with decreasing liquor ratio (owing to increasing values of L), then values of $[D_{sol}]_f$ increase
 591 accordingly. As the solubility of the reactive dye in bulk dyebath dye solution, $[D_{sol}]_s$, is reduced

592 when liquor ratio is lowered, it follows that term $([D] - [D_{sol}]_f/[D_{sol}]_s)$ will increase and, therefore, the
 593 dye concentration gradient (ie $[D_{sol}]_f/[D_{sol}]_s/L$) must also increase, so that a higher driving force for
 594 dyeing arises.

595

596 In effect, the increased uptake of reactive dyes that accompanies a reduction in the liquor ratio
 597 employed for dyeing is a process of controlled precipitation of the dye within the fibre. As such,
 598 reducing the liquor ratio used for dyeing is analogous to that of adding inorganic electrolyte to the
 599 dyebath, insofar as, both actions lower the concentration of dye in the dyebath solution phase.

600

601 It was shown (5), that Eq 4 explained why the use of very low liquor ratios enabled direct dyes to be
 602 applied in the complete absence of added NaCl or Na₂SO₄ because reducing the liquor ratio used
 603 for dyeing achieves the same outcome as adding inorganic electrolyte to the direct dye dyebath,
 604 namely promotion of dye uptake. Since, as discussed above, it is assumed that in the absence of
 605 dye-fibre reaction, the adsorption of reactive dyes on cellulosic fibres occurs in a manner analogous
 606 to that of direct dyes (7), then a similar situation should apply in the case reactive dye uptake on
 607 cotton.

608

609 4.1.2 an equation that relates to the final dye distribution at the end of dyeing

610 In the case of the model proposed for direct dyes on cellulosic fibres (4), the effect of liquor ratio on
 611 the final distribution of the dye between the fibre and dyebath phases at the end of an exhaust
 612 dyeing process can also be explained from a theoretical viewpoint in the context of the partition
 613 expressed by Eq 3. For this, Eq 6 was derived, where L is the fractional liquor ratio, as defined in Eq
 614 5.

615

$$616 \quad S = \frac{[D]_f}{[D]_s} = \left(\frac{[D] - \frac{[D]_s}{L}}{\frac{[D]_s}{L}} \right) \quad 6$$

617

618 The distinct dependency of final dye uptake (ie $[D]_f/[D]_s$) and thus the substantivity coefficient, S , on
619 dye solubility in the dyebath, $[D]_s$ described by Eq 4 is directly influenced by liquor ratio via the term
620 $[D]_s/L$ in Eq 6 (4) ; the same approach can be used to explain the effect of liquor ratio on reactive
621 dye uptake.

622

623 Eq 6 therefore describes the relationship between the distribution of the reactive dye, at the end of
624 dyeing, between the fibre, $[D]_f$, and solution, $[D]_s$, phases, expressed in terms of the substantivity
625 coefficient, S , and fractional liquor ratio, L . Liquor ratio directly effects the amount of reactive dye in
626 the dyebath rather than the amount of dye in the fibre insofar as, because of the term $([D]_s/L)$. As
627 liquor ratio is lowered, the effective concentration of dye in the dyebath (ie $[D]_s$) is also lowered
628 because of the term $([D]_s/L)$. It follows that the term $([D] - [D]_s/[D]_s)$ will therefore increase and the
629 dye concentration gradient (ie $[D]_f/[D]_s$) will increase accordingly, so that a higher driving force for
630 dyeing is developed.

631

632 From this it follows that it is the effect of liquor ratio on the amount of reactive dye in solution that
633 influences the partition of the dye between the fibre and solution phases.

634

635 4.1.3 comparison of the two models

636 Eq 4 and Eq 6 provide reasonable explanations for the promotional effect imparted by reduced
637 liquor ratio on reactive dye adsorption. For similar reasons to those recounted in section 3.2.1.3, the
638 two equations differ in terms of the particular stages of the dyeing process to which they apply and
639 the nature of the data that is required for their solution. Both models suggest that reactive dyeing
640 should be achievable in the complete absence of added inorganic electrolyte using low liquor ratios.

641

642 This is a focus of the work described in the next part of the paper. The results of dyeings carried out
643 on cotton produced using commercial grade reactive dyes at various liquor ratios in both the
644 absence and presence of added NaCl are interpreted in terms of the above model of reactive dye
645 uptake. It will be demonstrated that the effects of both added electrolyte and reduction in liquor ratio

646 are sufficiently well described using the model to explain why it is possible to obtain dyeings using
647 reactive dyes on cotton in the complete absence of added inorganic electrolyte.

648

649 **5 conclusions**

650 A model is proposed to account for the promotional effect imparted by added NaCl or Na₂SO₄ on
651 the uptake of reactive dyes on cellulosic fibres, which utilises the concept of interstitial water.
652 According to this model, which was based upon that previously developed for direct dyes on
653 cellulosic fibres, adding inorganic electrolyte to a reactive dye dyebath promotes dye uptake
654 because the electrolyte encourages dye aggregation in the dyebath, so that the inherent preference
655 of the dye to favour the aqueous phase shifts towards the fibre phase, which results in increased
656 dye uptake. It was shown that the same theoretical model could also explain the promotional effect
657 which reducing the liquor ratio used for dyeing has on the uptake of reactive dyes on cellulosic
658 fibres.

659

660 As such, the theoretical models describe both the motivational force that drives the transfer of the
661 reactive dye molecules from the dyebath to the fibre as well as the important combinatorial nature of
662 added inorganic electrolyte and liquor ratio in this transfer process, under conditions that represent
663 commercial dyeing (ie non-equilibrium).

664

665 In the next part of the paper, the theoretical model will be interrogated by determining whether it can
666 be used to interpret the results obtained for a series of dyeings on cotton which had been carried
667 out using commercial grade direct dyes, employing different liquor ratios in both the absence and
668 presence of added NaCl. Indeed, the next part of the paper will demonstrate how the theoretical
669 models explain why it is possible to secure uniform dyeings of the desired depth of shade on cotton
670 using commercial reactive dyes in the complete absence of added inorganic electrolyte.

671

672 **References**

- 673 1. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 1 Dyes
674 and Pigments. 2017; in press.
- 675 2. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 2
676 analysis of conventional models that describe the manner by which inorganic electrolytes promote direct dye
677 uptake on cellulosic fibres. *Dyes and Pigments*. 2017; in press.
- 678 3. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 3
679 theoretical model to describe the role of inorganic electrolytes used in dyeing cellulosic fibres with direct dyes.
680 *Dyes and Pigments*. 2017; in press.
- 681 4. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 4
682 theoretical model to describe the role of liquor ratio in dyeing cellulosic fibres with direct dyes in the presence
683 of inorganic electrolytes. *Dyes and Pigments*. 2017; in press.
- 684 5. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 5
685 inorganic electrolytes used in dyeing cotton with commercial grade reactive dyes. ??? 2017;?
- 686 6. Burkinshaw SM, Salihu G. The role of auxiliaries in the immersion dyeing of textile fibres: Part 6
687 analysis of conventional models that describe the manner by which inorganic electrolytes promote reactive
688 dye uptake on cellulosic fibres. *Dyes and Pigments*. 2017; in press.
- 689 7. Burkinshaw SM. *Physico-chemical aspects of textile coloration*. Chichester: Wiley; 2016.
- 690 8. Anon. *Textile Effects: Novacron FN reactive dyes; warm exhaust dyeing*. Huntsman Textile Effects
691 122007e: July 2007: Huntsman 2008.
- 692 9. Han HK, Jung H-K. Solubility and growth rate of reactive blue49 and black8 dyes in salting-out
693 system. *Korean Journal of Chemical Engineering*. 2009 2009//;26(1):246-9.
- 694 10. Madan GL, Shrivastava SK. *Physical Chemistry of Dyeing of Cellulosic Fibers with Reactive Dyes:
695 Part I : The Role of Electrolytes in the Sorption of Hydrolyzed Reactive Dyes*. *Textile Research Journal*. 1979
696 June 1, 1979;49(6):322-5.
- 697 11. Hamlin JD, Phillips DAS, Whiting A. UV/Visible spectroscopic studies of the effects of common salt
698 and urea upon reactive dye solutions. *Dyes and Pigments*. 1999;41(1-2):137-42.
- 699 12. Dizge N, Aydiner C, Demirbas E, Kobya M, Kara S. Adsorption of reactive dyes from aqueous
700 solutions by fly ash: Kinetic and equilibrium studies. *Journal of Hazardous Materials*. 2008;150(3):737-46.
- 701 13. Al-Degs YS, El-Barghouthi MI, El-Sheikh AH, Walker GM. Effect of solution pH, ionic strength, and
702 temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and Pigments*. 2008;77(1):16-
703 23.
- 704 14. Şayan E. Optimization and modeling of decolorization and COD reduction of reactive dye solutions by
705 ultrasound-assisted adsorption. *Chemical Engineering Journal*. 2006;119(2-3):175-81.
- 706 15. Netpradit S, Thiravetyan P, Towprayoon S. Adsorption of three azo reactive dyes by metal hydroxide
707 sludge: effect of temperature, pH, and electrolytes. *Journal of Colloid and Interface Science*. 2004;270(2):255-
708 61.
- 709 16. Burkinshaw SM. Non-aqueous treatment method: WO2006040539 A1. 2004.
- 710 17. Burkinshaw SM, Negrou AM. The wash-off of dyeings using interstitial water part 1: Initial studies.
711 *Dyes and Pigments*. 2011;90(2):177-90.
- 712 18. Burkinshaw SM, Howroyd J, Kumar N, Kubambe O. The wash-off of dyeings using interstitial water
713 Part 2: bis(aminochlorotriazine) reactive dyes on cotton. *Dyes and Pigments*. 2011;91:134-44.
- 714 19. Burkinshaw SM, Howroyd J, Kumar N, Kabambe O. The wash-off of dyeings using interstitial water:
715 Part 3. Disperse dyes on polyester. *Dyes and Pigments*. 2011;91(3):340-9.
- 716 20. Burkinshaw SM, Salihu G. The wash-off of dyeings using interstitial water: Part 4 Disperse and
717 reactive dyes on polyester/cotton fabric. *Dyes and Pigments*. 2013;99:548-60.
- 718 21. Bradbury MJ, Collishaw PS, Moorhouse S. Reactive Dye Selection and Process Development for
719 Exhaust Dyeing of Cellulose. *Textile Chemist & Colorist*. 1995(8):19-23.
- 720 22. Bradbury M, Collishaw P, Moorhouse S. Dynamic responsendasprocess optimisation in the exhaust
721 dyeing of cellulose. *Journal of the Society of Dyers and Colourists*. 1995;111(5):130-4.
- 722 23. Bent CJ, Davies PA, Phillips DAS. Latest Developments in the Batchwise Application of Hot-dyeing
723 Reactive Dyes to Cellulosic Knitwear. *Journal of the Society of Dyers and Colourists*. 1982;98(10):326-34.
- 724 24. Lidyard AM, Woodcock A, Noone P. Economic considerations from the exhaust application of reactive
725 dyes under ultra-low liquor ratio conditions*. *Journal of the Society of Dyers and Colourists*. 1992;108(11):501-
726 4.
- 727 25. Gorenssek M, Gaber V, Peternelj N, Vrhunc V. The influence of liquor ratio on the jet dyeing of
728 cellulose fibres using different types of monochlorotriazine reactive dyes. *Journal of the Society of Dyers and
729 Colourists*. 1995;111(1-2):19-21.
- 730

ACCEPTED MANUSCRIPT

Highlights

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

ACCEPTED MANUSCRIPT