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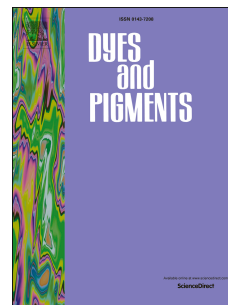
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Accepted Manuscript

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

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

5
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10

11 **Abstract**

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

20

21 **Highlights**

- 22 • the role of liquor ratio in direct 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 **keywords**

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

28

29 **1 Introduction**

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

35

36 In recognition of the global popularity of cotton and other cellulosic fibres, the previous two parts of
37 the paper (2, 3) considered the role of the most important auxiliary used in the dyeing of cellulosic
38 fibres, namely NaCl or Na₂SO₄. Although very large amounts of inorganic electrolyte are habitually
39 added to direct dye dyebaths to promote dye uptake onto cellulosic fibres, the precise nature of the
40 promotional effect imparted by NaCl or Na₂SO₄ has not been entirely resolved, despite considerable
41 research interest over many decades. As conventional models of direct dye adsorption cannot
42 adequately account for either the inherently low uptake of direct dyes on cellulosic fibres in the
43 absence of added inorganic electrolyte nor the marked ability of NaCl and Na₂SO₄ to promote dye
44 uptake, a theoretical model was proposed to explain the promotional effect of added inorganic
45 electrolyte on the uptake of direct dyes on cellulosic fibres, which utilised the concept of interstitial
46 water (3). According to this model, the inherently low substantivity displayed by direct dyes towards
47 cellulosic fibres in the absence of added electrolyte is attributable to the dye's marked preference for
48 the aqueous dyebath phase, which stems from the dye's high aqueous solubility. Adding NaCl or
49 Na₂SO₄ to a direct dye dyebath encourages dye aggregation which reduces the solubility of the dye
50 in the dyebath phase, so that the intrinsic preference of the previously highly soluble dye to favour
51 the aqueous phase shifts towards the fibre phase and so dye uptake is promoted.

52

53 In this part of the paper, the previously recounted theoretical model of the promotional effect
54 imparted by added inorganic electrolyte on dye uptake (3) will be utilised to develop a model that

55 seeks to explain the manner by which reducing the liquor ratio used for dyeing promotes the uptake
56 of direct dyes on cellulosic fibres.

57

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

65

66 **2 conventional models of direct dye adsorption on cellulosic fibres**

67 As previously recounted (2, 3), the mechanism by which direct dyes are adsorbed onto cellulosic
68 fibres is interpreted conventionally using Eq 1 (and equations based on this), which describes the
69 partition of dye between the fibre phase and the solution phase when equilibrium dye uptake has
70 been achieved (ie when dye adsorption and dye desorption processes are equal), where $[D]_f$ is the
71 amount of dye present in the fibre phase (ie the substrate) relative to the amount of fibre and $[D]_s$ is
72 the amount of dye in solution (ie the dyebath) relative to the amount of solution.

73

$$74 \quad K = \frac{[D]_f}{[D]_s} \quad 1$$

75

76 The equilibrium partition coefficient, K , describes the distribution of the dye between the dyebath, s
77 and fibre, f , phases; the higher the value of K the greater is the partition of the dye in favour of the
78 fibre phase (ie $[D]_f > [D]_s$) and the greater is the extent of dye uptake onto the substrate.

79

$$80 \quad -\Delta\mu^0 = RT \ln \frac{[Na^+]_f^z [D^-]_f}{v^{z+1} [Na^+]_s^z [D^-]_s} \quad 2$$

81

82 Variants of Eq 1, such as Eq 2 (4), are widely used to express the partition of the dye between the
83 fibre and solution phases at the end of equilibrium dyeing in terms of the thermodynamic standard
84 affinity of the dye, $-\Delta\mu^\theta$ (5). However, the approach adopted in using equations such as Eq 2, suffers
85 several shortcomings, as discussed previously (2, 3), insofar as it provides no meaningful
86 information about the dyeing process prior to equilibrium, nor does it offer explanations as to why
87 direct dyes display inherently low substantivity towards cellulosic fibres in the absence of added
88 inorganic electrolyte or why NaCl or Na₂SO₄ are so effective in promoting dye uptake. Of relevance
89 to this part of the paper, conventional models of direct dye adsorption on cellulosic fibres are unable
90 to account for the promotional effect imparted by reduced liquor ratio on dye uptake.

91

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

98

99 It is of interest to note that many of the findings of the various researchers referred to in both this
100 and the previous part of this paper (3) were the result of meticulous, elegant and, at the time,
101 transformational studies on dyeing. However, these observations were made when the liquor ratio
102 employed for dyeing was not considered as being in any way problematic from either economic,
103 technical or environmental perspectives, because, at the time, water was plentiful and (relatively)
104 cheap; consequently, dyeing machines customarily operated at very long liquor ratios. Indeed, it
105 wasn't until the oil crises of 1973 and 1980 and the resulting increased costs of heating (as well as
106 evaporating, pumping, etc.) the very large volumes of water that were habitually employed in
107 exhaust dyeing processes, that both industrial practice and research effort began to focus on ways
108 of reducing water usage and, therefore, liquor ratio became of major importance. Thus, the findings
109 reported in many earlier studies concerning the effects of added electrolyte on direct dye adsorption

110 often were obtained using very long liquor ratios (eg 1:40 or greater) and the crucially important
 111 combinatorial nature of the effects of added inorganic electrolyte and reduced liquor ratio on direct
 112 dye uptake received little, if any, attention.

113

114 3 liquor ratio

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

123

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

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

126

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

130

131 The particular liquor ratio that is utilised in immersion dyeing varies according to, for instance, type
 132 of dye, type of fibre, fibre construction, machine type, etc. For example, contemporary jet dyeing
 133 machines used for knitted cotton fabrics typically employ a 1:8 – 1:10 liquor ratio whereas in the

134 case of *Best Available Technology* (BAT) jet machines, a liquor ratio of 1:4.5 - 1:5 is common.
 135 Liquor ratio influences both the rate and extent of dye uptake, as well as the amount of auxiliaries
 136 that are employed, when dyeing recipes are based on liquor ratio rather than omf (1).

137

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

149

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

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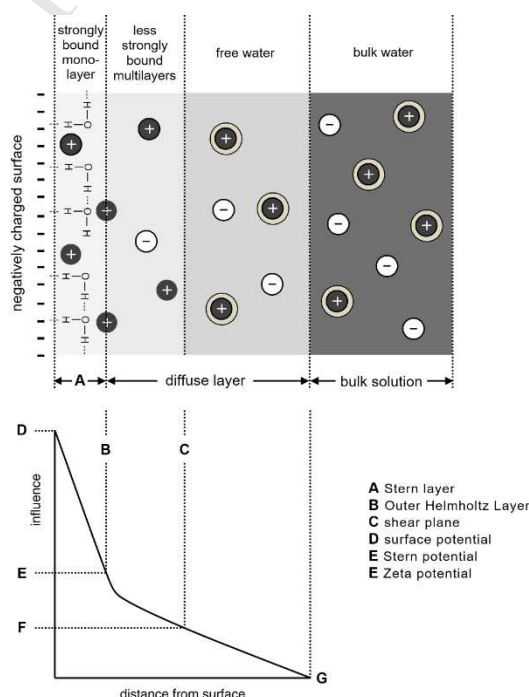
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162

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

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

168

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

175

176 **4 a model to explain the effect of liquor ratio on the adsorption of direct dyes on cellulosic**
 177 **fibres**

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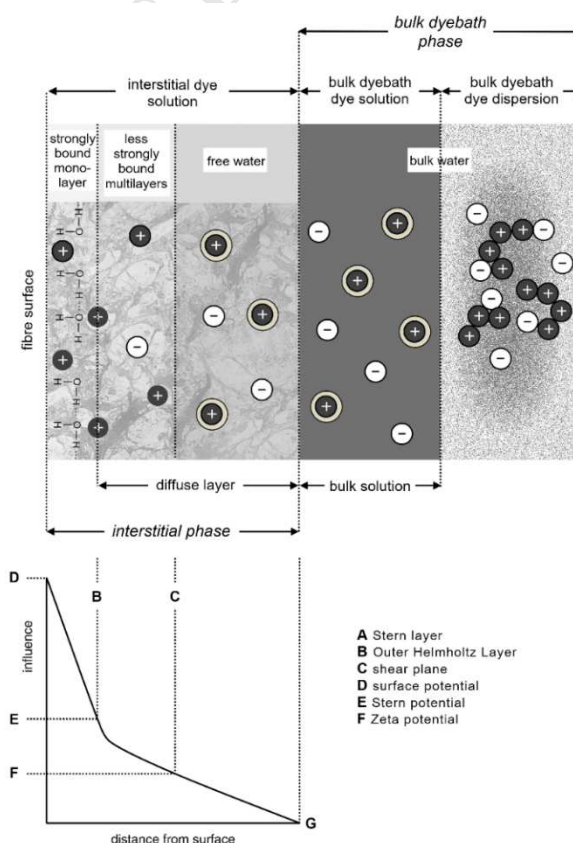
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190

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

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

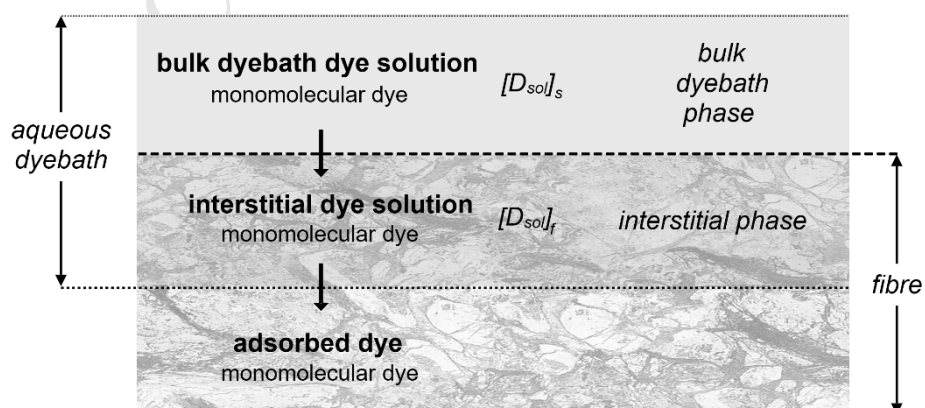
200

201 4.1 interstitial water

202 According to the concept of interstitial water, which has previously been invoked in the development
203 of an immersion dyeing process (7) and a wash-off process for dyeings (8-11), interstitial water
204 provides functions that differ to those afforded by the remaining bulk water, such as heating,
205 agitation, etc. that are required for immersion dyeing. The volume of interstitial water present within
206 a textile substrate can be assumed to correspond to the moisture regain of the substrate at 100%
207 Relative Humidity, RH , which, by way of example, in the case of cotton, corresponds to 0.22 l kg^{-1}
208 (11).

209

210



217

Figure 3 representation of interstitial dyeing mechanism (3)

218

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

227

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

238

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

246 relative to the total amount of water used for dyeing, decreases markedly, with increasing liquor
247 ratio.

248

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

255

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

262

263 *4.2 the roles of dye diffusion and dye-fibre substantivity in direct dye adsorption*

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

272

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

284

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

288

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

294

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

301 molecules have upon dye-fibre interactions, dye-fibre substantivity is a mostly unresolved
302 phenomenon (5).

303

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

314

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

327

328 Despite the simplicity of this particular interpretation of the complex and little understood
329 phenomenon of dye-fibre substantivity, a theoretical model was devised based upon this
330 interpretation, which provided a practical explanation for the promotional effect imparted by added
331 NaCl or Na₂SO₄ in the adsorption of direct dyes on cellulosic fibres. The model assumed that the
332 aqueous solubility of a direct dye is the main contributor to dye-fibre substantivity and demonstrated
333 that the solubility of the dye in the bulk dyebath phase determines the distribution of the dye
334 between the fibre and dyebath phases (ie determines the extent of dye uptake) (3). The model was
335 shown to be valid for dyeing carried out with the intention of achieving either non-equilibrium dye
336 adsorption (ie commercial dyeing processes) or equilibrium dye adsorption and provided an
337 explanation as to why the transfer of direct dye molecules from the aqueous phase to the fibre
338 phase continues once the driving force provided by dye diffusion has ceased (3).

339
340 The model (3) revealed that the high aqueous solubility of direct dyes is responsible for not only
341 their inherently low substantivity towards cellulosic fibres when applied in the absence of added
342 inorganic electrolyte, but also, why added NaCl or Na₂SO₄ is so remarkably successful in promoting
343 dye uptake. It was considered (3) that in the absence of added inorganic electrolyte, the dye prefers
344 to remain in the aqueous dyebath phase rather than transfer to the fibre phase, because of the
345 dye's high aqueous solubility. Adding inorganic electrolyte to a direct dye dyebath encourages dye
346 aggregation which reduces the solubility of the dye in the dyebath phase, so that the intrinsic
347 preference of the previously highly soluble dye to favour the aqueous phase shifts towards the fibre
348 phase and so dye uptake is promoted (3).

349
350 Such a model seems to be of interest from the viewpoint of the liquor ratio used in dyeing, since a
351 reduction in liquor ratio will reduce the amount of water available for dye dissolution, which can be
352 assumed will have implications in terms of dye solubility and, thus, the extent of dye uptake. Indeed,
353 as will be demonstrated below, the theoretical model (3) proposed to explain the promotional effect
354 imparted by added NaCl or Na₂SO₄ on the adsorption of direct dyes on cellulosic fibres can be
355 employed to describe the promotional effect of reduced liquor ratio on direct dye uptake.

356

357 *4.3 the use of two equations to describe the effect of liquor ratio on direct dye adsorption*

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

365

366 4.3.1 an equation that applies to dye uptake during immersion dyeing

367 According to the idea that dyeing takes place from within interstitial dye solution, as depicted by
 368 Figure 3, Eq 3 was derived to explain the promotional effect on direct dye uptake imparted by added
 369 NaCl or Na₂SO₄ (3), in which $[D]$ is the total amount of dye within the immersion dyeing system,
 370 which comprises dye that is present in the interstitial dye solution within the fibre phase, $[D_{sol}]_f$
 371 together with that present in the bulk dyebath dye solution in the dyebath phase, $[D_{sol}]_s$, and S is the
 372 substantivity coefficient.

373

$$374 \quad S = \frac{[D_{sol}]_f}{[D_{sol}]_s} = \left(\frac{[D] - [D_{sol}]_s}{[D_{sol}]_s} \right) \quad 3$$

375

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

383 $[D_{sol}]_s$. From Eq 3 it is evident that because of the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$, the degree of substantivity
384 displayed by the dye towards the fibre, as represented by the substantivity coefficient, S , is
385 determined by the concentration of dye in solution within the bulk dyebath, $[D_{sol}]_s$, relative to the total
386 amount of dye within the dyeing system, $[D]$; the greater this difference, the higher is dye-fibre
387 substantivity, and, therefore, the greater the extent of dye uptake.

388

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

393

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

408

409 When dyeing is carried out in the presence of added NaCl or Na_2SO_4 , the aqueous solubility of the
410 direct dye will be reduced because of electrolyte-induced aggregation. Thus, according to Eq 3, the

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

418

419 4.3.1.1 the ability of the equation to predict changes in dye-fibre substantivity imparted by reduced
420 liquor ratio

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

425

426 As the liquor ratio employed for dyeing increases, so $[D_{sol}]_s$ will increase because more water is
427 available for a given amount of dye to dissolve; in contrast, $[D_{sol}]_s$ will decrease with decreasing
428 liquor ratio because less water is available for a given amount of dye to dissolve. The last statement
429 can be explained by reference to the marked propensity of direct dyes to aggregate in aqueous
430 solution via coplanar association, and the fact that this particular attribute of direct dyes is
431 encouraged in solutions of high dye concentration (2). When the liquor ratio of the dyebath is
432 reduced, because the amount of water in which the direct dye molecules can dissolve is lowered,
433 then the initial dye concentration in the dyebath will be increased correspondingly. Owing to the
434 planar nature of direct dye anions and the likelihood of π - π interactions operating between aromatic
435 centres within neighbouring dye molecules, which are responsible for the well-known tendency of
436 direct dyes to aggregate in aqueous solution, the combined effects of reduced dyebath volume (ie
437 amount of water available for dye dissolution) and greater initial dye concentration in the dyebath
438 will encourage dye aggregation. Such aggregates will have lower aqueous solubility than their

439 monomolecular direct dye counterparts owing to strong dye-dye interactions between neighbouring
440 dye molecules and suppressed ionisation of the dye molecules, that are promoted by hydrophobic
441 interaction and the requirement of the water molecules that surround the dye solute molecules to
442 minimise their interaction with the amphiphilic direct dye solutes and so reduce the disruption of the
443 surrounding water structure by the dye molecules (2). Therefore, reducing the liquor ratio used for
444 dyeing can be considered as a dilution factor because hydrophobic interaction results in reduced
445 dye solubility and so the concentration of dye in the dyebath (ie $[D_{sol}]_s$) is lowered.

446

447 As discussed, in Eq 3, the substantivity coefficient, S (ie $[D_{sol}]_f/[D_{sol}]_s$) describes the relative
448 preference of the dye towards the fibre and dyebath phases; the higher the value of this ratio then
449 the greater is the preference of the dye in favour of the fibre phase (ie $[D_{sol}]_f > [D_{sol}]_s$) and, therefore,
450 the greater is the extent of dye adsorption on the fibre. Since the magnitude of the substantivity
451 coefficient is determined by the difference between the concentration of dye in solution in the bulk
452 dyebath, $[D_{sol}]_s$, relative to the total amount of dye within the dyeing system, $[D]$, via the term $([D] -$
453 $[D_{sol}]_s/[D_{sol}]_s)$, it follows that at high liquor ratios, $[D_{sol}]_s$ will be high and therefore, the term $([D] -$
454 $[D_{sol}]_s/[D_{sol}]_s)$ will be low, so that the substantivity coefficient, $[D_{sol}]_f/[D_{sol}]_s$, will be correspondingly low
455 and dye uptake will not be favoured, as observed in practice, owing to the direct dye's preference to
456 remain within the aqueous dyebath phase. In contrast, at low liquor ratios, $[D_{sol}]_s$ will be reduced, so
457 that the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$ will increase, resulting in a high substantivity coefficient, $[D_{sol}]_f/[D_{sol}]_s$,
458 so that dye uptake will be promoted, as also fits with practical observation.

459

460 Hence, the observed promotion of direct dye uptake onto cellulosic fibres imparted by lowering the
461 liquor ratio employed for dyeing can be explained in terms of the combined effects which increased
462 dye aggregation and reduced dye solubility have upon the substantivity coefficient, $[D_{sol}]_f/[D_{sol}]_s$.
463 Lowering liquor ratio encourages dye aggregation which reduces the solubility of the dye in the
464 dyebath phase, so that the intrinsic preference of the previously highly soluble direct dye to favour
465 the aqueous phase shifts towards the fibre phase and so dye uptake is promoted. As discussed, this

466 particular model was also advanced to describe the promotional effect of added inorganic electrolyte
467 on the uptake of direct dyes on cotton and other cellulosic fibres (3).

468

469 By way of illustration, let us assume that 1 kg of cotton (moisture regain = 0.22 l kg⁻¹) is to be dyed
470 to a 5% omf depth of shade using a pure sample of C.I. Direct Yellow 12, which has an aqueous
471 solubility of 7.61 gl⁻¹ that is reduced to 0.19 gl⁻¹ and 0.069 gl⁻¹ in the presence of 4 gl⁻¹ and 10 gl⁻¹
472 NaCl, respectively (12). If a 1:8 liquor ratio is employed for dyeing then because 22% of the dyebath
473 volume (ie 1.76 l) will comprise interstitial dye solution within the fibre phase, $[D_{sol}]_f$, the volume of
474 the dye solution in the bulk dyebath phase, $[D_{sol}]_s$, will be 6.24 l. As a 5% omf shade is to be applied
475 (ie 50 g of dye for the 1 kg of cotton), the concentration of dye within the immersion dyeing system,
476 $[D]$, will be 6.25 gl⁻¹, which is within the aqueous solubility limit of the dye (ie 7.61 gl⁻¹).

477

478 In the case of dyeing in the absence of added NaCl or Na₂SO₄, if it is assumed that no self-
479 association of the dye molecules occurs, the amount of dye in the dye solution within the 6.24 l bulk
480 dyebath phase, $[D_{sol}]_s$, will be 4.88 gl⁻¹ (ie 6.24/8 * 6.25 gl⁻¹) which is again within the solubility of the
481 dye in water (ie 7.61 gl⁻¹). Thus, from Eq 3, the substantivity coefficient, $S = [D_{sol}]_f / [D_{sol}]_s = 0.28$ (ie
482 $([D] - [D_{sol}]_s) / [D_{sol}]_s = 0.28$) and, therefore, at a liquor ratio of 1:8, the partition of the dye between the
483 dyebath and solution phases will favour the fibre phase, but only to a relatively small extent because
484 of the dye's high solubility in water (in the absence of added inorganic electrolyte) and the
485 preference of the dye for the bulk aqueous dyebath phase, $[D_{sol}]_s$. Thus, the innate tendency of the
486 direct dye molecules to move from the dyebath phase to the fibre phase under the presence of a
487 dye concentration gradient (ie according to diffusion) will receive a moderate boost from dye-fibre
488 substantivity, although the overall level of substantivity displayed by the dye towards the cellulosic
489 substrate will still be low, because of the dye's high solubility in the dyebath.

490

491 Let us now consider that the 5% omf dyeing of cotton using purified C.I. Direct Yellow 12 in the
492 absence of added inorganic electrolyte are to be repeated but instead using liquor ratios of 1:4 and
493 1:1. Because the amount of water in the dyebath will decrease with decreasing liquor ratio, so the

494 values of both $[D]$ and $[D_{sol}]_s$ will increase correspondingly, compared to that which prevailed when
 495 dyeing had been carried out using a 1:8 liquor ratio (ie $[D] = 6.25 \text{ gl}^{-1}$ and $[D_{sol}]_s = 4.88 \text{ gl}^{-1}$). Thus,
 496 for the 1:4 and 1:1 liquor ratio dyebaths, the values of $[D]$ will be 12.5 gl^{-1} and 50 gl^{-1} , respectively
 497 and the corresponding values of $[D_{sol}]_s$ will be 9.75 gl^{-1} and 39.0 gl^{-1} , respectively. However, as the
 498 $[D_{sol}]_s$ values are greater than the solubility of the dye in the absence of added inorganic electrolyte
 499 (ie 7.61 gl^{-1}), the maximum concentration of dye in the bulk dyebath dye solution, $[D_{sol}]_s$ can only be
 500 7.61 gl^{-1} and the remaining dye must therefore be present in the form of aggregates. Thus, from Eq
 501 3, values for $S = 0.64$ and 5.57 are secured when dyeing is undertaken using liquor ratios of 1:4 and
 502 1:1, respectively. In these cases, the tendency of the direct dye molecules to move from the dyebath
 503 to the fibre under the influence of a dye concentration gradient (ie according to diffusion) will receive
 504 a more meaningful boost from dye-fibre substantivity, because of the dye's reduced solubility in the
 505 dyebath.

506

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

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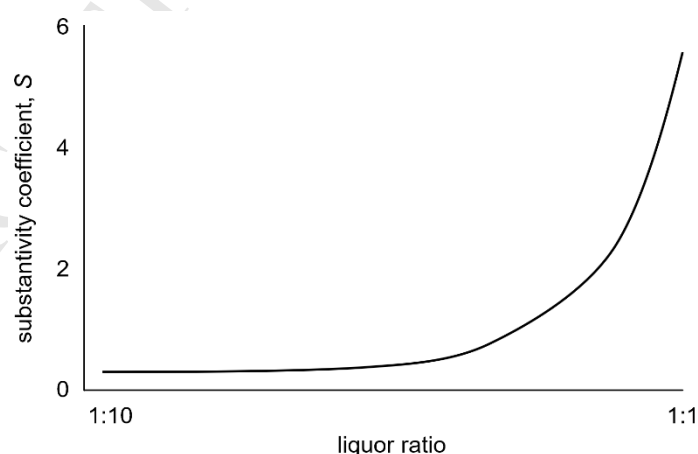
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520 Figure 4 substantivity coefficient, S as a function of liquor ratio for C.I. Direct Yellow 12 in the absence of
 521 added inorganic NaCl using Eq 3



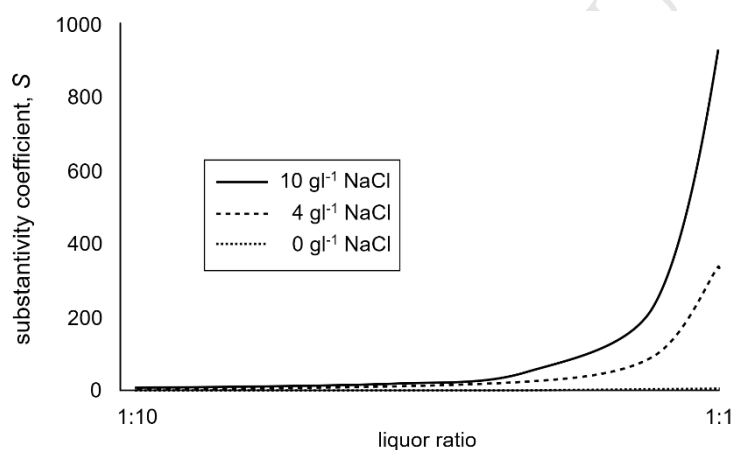


Figure 5 substantivity coefficient, S as a function of liquor ratio for C.I. Direct Yellow 12 in the presence and absence of added NaCl calculated using Eq 3

As mentioned, Eq 3 was originally derived to explain the promotional effect on direct dye uptake imparted by added inorganic electrolyte. As such, Eq 3 therefore describes the combined effects which liquor ratio and added NaCl or Na_2SO_4 impart to direct dye uptake. When the above calculations were repeated but, in this case, assuming that C.I. Direct Yellow 12 was applied over the range of 1:10 to 1:1 liquor ratios in both the absence and presence of 4 g l^{-1} and 10 g l^{-1} NaCl, again using the dye solubility data of reference (12), the data displayed in Figure 5 were secured. As Figure 5 reveals, Eq 3 predicts that dye uptake, expressed via the substantivity coefficient, S ,

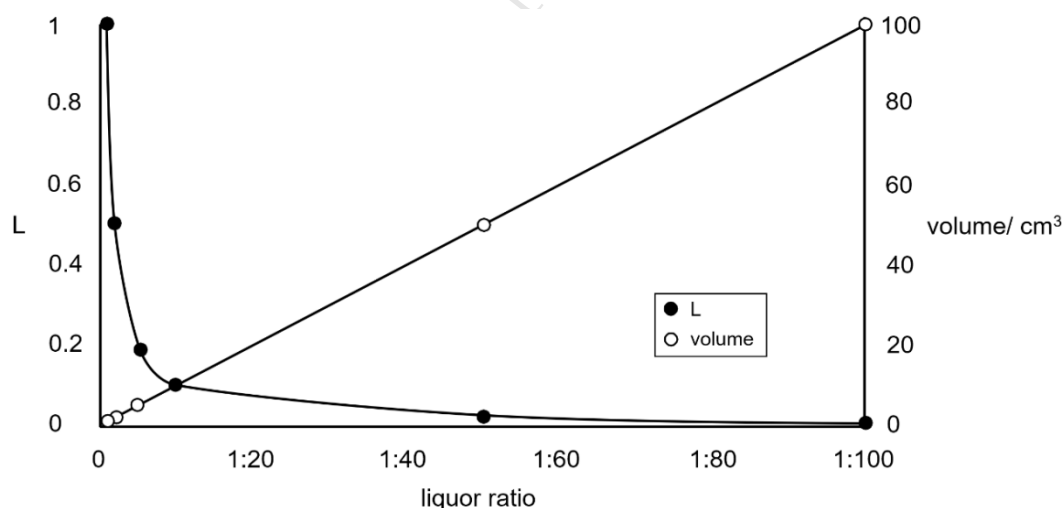
550 increases with both decreasing liquor ratio and increasing amount of added inorganic electrolyte, as
 551 fits with practical observation, because reducing the liquor ratio used for dyeing and adding either
 552 Na_2SO_4 or NaCl to a direct dyebath each result in reduced dye solubility, as described by Eq 3.

553

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

563

564



571

572 Figure 6 variation of fractional liquor ratio, L and dyebath volume as a function of liquor ratio over the range

573

1:1 to 1:100

574

575 The relationship between the promotional effect of reduced liquor ratio on direct dye uptake
 576 expressed via dye solubility, as described in Eq 3, can be further articulated, quantitatively, by
 577 modifying Eq 3. Because liquor ratio is a fraction, as exemplified by $1/5$, $1/10$, etc. then values of the

578 fractional liquor ratio, L , increase with decreasing liquor ratio. For example, values of L (units of L
 579 will be mass (of fibre) per unit volume (of dyebath), such as kg l^{-1}) increase from 0.01 in the case of
 580 a 1:100 liquor ratio, through 0.02 for a liquor ratio of 1:50, 0.1 for a 1:10 liquor ratio through to 0.2 for
 581 a liquor ratio of 1:5, as illustrated by the exponential curve shown in Figure 6 for liquor ratios varying
 582 from 1:1 to 1:100.

583

$$584 \quad L = \frac{m}{v} \quad 4$$

585

$$586 \quad [D] = [D_{sol}]_f m + [D_{sol}]_s v \quad 5$$

587

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

595

596 Substituting from Eq 5 into Eq 3 provides Eq 6.

597

$$598 \quad S = \frac{[D_{sol}]_f m}{[D_{sol}]_s v} = \left(\frac{[D] - [D_{sol}]_s v}{[D_{sol}]_s v} \right) \quad 6$$

599

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

601

$$602 \quad v = \frac{m}{L} \quad 7$$

603

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

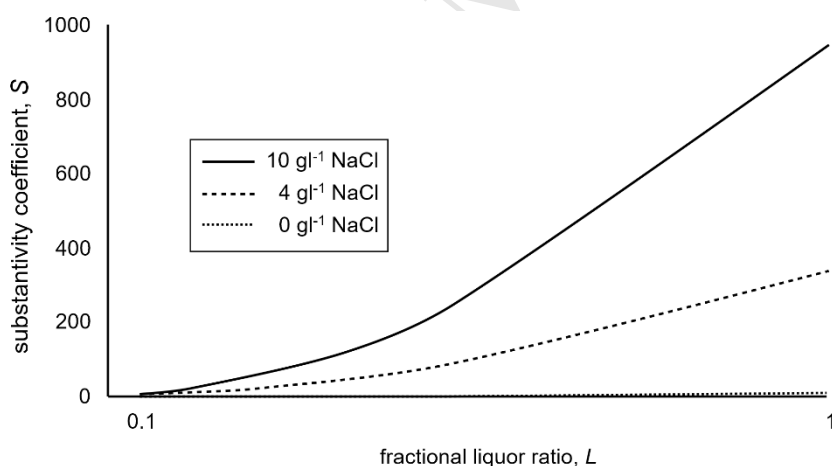
605

606 Owing to the term $([D_{sol}]_s/L)$ in Eq 8, liquor ratio, via L , impacts directly on the amount of dye in
 607 solution in the bulk dyebath phase, $[D_{sol}]_s$, rather than on the amount of dye in the interstitial solution
 608 in the fibre, $[D_{sol}]_f$. This is because values of $[D_{sol}]_s$ will decrease markedly with decreasing liquor
 609 ratio since values of L increase with decreasing liquor ratio (eg value of L @ a given liquor ratio:
 610 0.01 @ 1:100; 0.02 @ 1:50; 0.1 @ 1:10; 0.2 @ 1:5; 1 @ 1:1) and, therefore, values of $[D_{sol}]_f$ will
 611 decrease accordingly.

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

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

To illustrate this, Figure 7 shows a plot of S as a function of fractional liquor ratio, L , assuming that C.I. Direct Yellow 12 was applied over the range $L = 0.1$ to 1 (corresponding to a liquor ratio range

630 of 1:10 to 1:1) in both the absence and presence of 4 g l^{-1} and 10 g l^{-1} NaCl, again using the dye
 631 solubility data of reference (12).

632

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

642

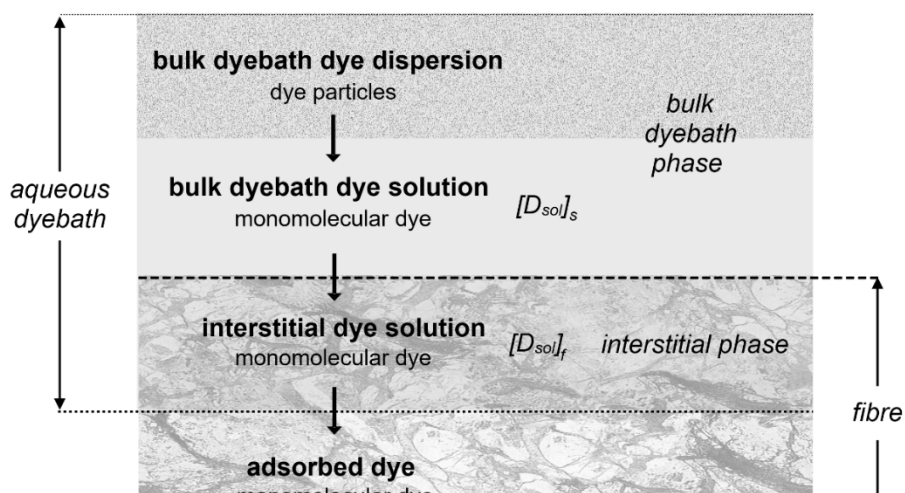
643 In effect, both Eq 3 and Eq 8 suggest that the observed increased uptake of direct dyes that
 644 accompanies a reduction in the liquor ratio employed for dyeing is a process of controlled
 645 precipitation of the dye within the fibre, since the solubility of the dye in the dyebath is reduced and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

648

649 4.3.1.2 the influence of liquor ratio in the context of an interstitial dyeing mechanism

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

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Figure 8 representation of direct dyeing mechanism (3)

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

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

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

692

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

703

704 Thus, this model, which utilises the concept of interstitial water, is analogous to that proposed to
705 account for the promotional effect imparted to direct dye uptake imparted by adding NaCl or Na₂SO₄
706 to a direct dye dyebath. Both models therefore predict that adding inorganic electrolyte and reducing
707 the liquor ratio used for dyeing have the same outcome, namely, that dye uptake is promoted
708 because dye aggregation in the dyebath is encouraged, as a result of which, the solubility of the dye
709 in the dyebath is reduced, so that, according to both Eq 3 and Eq 8, the substantivity coefficient,
710 $[D_{sol}]/[D_{sol}]_s$, will increase and dye uptake will be favoured, as is observed in practice.

711

712 Such a finding has important consequences, as it implies that reducing the liquor ratio used for
713 dyeing and adding inorganic electrolyte to a direct dye dyebath have a combinatorial effect upon

714 dye uptake, in that both actions exert similar influences upon dye-fibre substantivity which indeed
715 fits with practical observations. Thus, the supposition implicit in both Eq 3 and Eq 8, that direct dye
716 uptake is related to the solubility of the dye in the dyebath, concurs with the previously mentioned
717 practical dyebath behaviour that the adjustment of dye-fibre substantivity by manipulating physical
718 factors and physico-chemical aspects, has one aim, namely, to regulate dye solubility.

719
720 However, both Eq 3 and Eq 8 only relate the solubility of the direct dye to its likely distribution
721 between the interstitial dye solution in the fibre phase and the bulk dye solution in the dyebath
722 phase, which does not take into account the contribution of other dyebath variables that contribute
723 to dye-fibre substantivity (eg temperature, dyebath-fibre interchange rate, etc.). The values of the
724 substantivity coefficient, S (ie $[D_{sol}]_f / [D_{sol}]_s$) obtained using Eq 3 and Eq 8 are therefore indicative
725 only, insofar as, a high value of S implies that reduced dye solubility in the dyebath promotes dye
726 uptake whilst a low value of S suggests that high dye solubility in the dyebath demotes dye uptake.

727

728 4.3.2 an equation that relates to the final distribution of dye at the end of dyeing

729 Assuming that dye solubility is the key determinant of dye-fibre substantivity and, also, that the
730 solubility of the dye in the dyebath phase determines the relative partition of the dye between the
731 fibre and dyebath phases (ie the extent of dye uptake), it is possible to interpret the effect of liquor
732 ratio on the distribution of the dye between the fibre and dyebath phases that is achieved at the end
733 of an immersion dyeing process, using the partition described by Eq 1, as was previously
734 demonstrated in the case of added inorganic electrolyte (3). This particular approach will be shown
735 below to be of practical use, as it enables previously published data concerning the effect of
736 reduced liquor ratio on the (final) uptake of direct dyes on cellulosic materials, to be analysed from
737 the viewpoint of establishing the manner by which reduced liquor ratio in the presence of a constant
738 amount of added inorganic electrolyte promotes dye uptake.

739

740 Eq 9 was derived to explain the promotional effect on final direct dye uptake imparted by added
741 NaCl or Na₂SO₄ (3), in which $[D]$ is the total amount of dye within the immersion dyeing system, $[D]_f$

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

745

746

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

9

747

748 The ratio $[D]_f/[D]_s$ in Eq 9 describes the relative partition of the dye between the fibre and dyebath
 749 phases: the higher the value of this ratio then the greater is the partition of the dye in favour of the
 750 fibre phase (ie $[D]_f > [D]_s$) and the greater is the extent of dye uptake onto the substrate. As such,
 751 the ratio $[D]_f/[D]_s$ represents the substantivity displayed by the direct dye towards the substrate,
 752 which is expressed by the *substantivity coefficient* of the direct dye at the end of the immersion
 753 dyeing process, S . Owing to the term $([D] - [D_{sol}]_s/[D_{sol}]_s)$, the magnitude of S depends upon the
 754 amount of dye in the bulk dyebath dye solution, $[D_{sol}]_s$ relative to the total amount of dye within the
 755 dyeing system, $[D]$; the greater this difference in dye concentration, the higher is dye-fibre
 756 substantivity, and, therefore, the greater the extent of dye uptake.

757

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

767

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

771

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

781

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

784

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

787

$$788 \quad [D] = [D]_f m + [D]_s v \quad 10$$

789

790 Substituting into Eq 9 gives Eq 11.

791

$$792 \quad S = \frac{[D]_f m}{[D]_s v} = \left(\frac{[D] - [D]_s v}{[D]_s v} \right) \quad 11$$

793

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

795

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

12

797

798 Eq 12 therefore defines the relationship between the distribution of the dye between the fibre, $[D]_f$,
 799 and solution, $[D]_s$, phases, expressed in terms of the substantivity coefficient, S , and fractional liquor
 800 ratio, L . In terms of the partition of the dye between the fibre and dyebath phases, as described by
 801 the ratio $[D]_f/([D]_s/L)$, owing to the term $([D]_s/L)$ it is apparent that liquor ratio impacts directly on the
 802 amount of dye in solution rather than on the amount of dye in the fibre insofar as, values of $[D]_s$ will
 803 decrease with decreasing liquor ratio and, therefore, values of $[D]_f$ will increase accordingly. For
 804 example, because values of L increase with decreasing liquor ratio (eg $L = 0.02$ at a liquor ratio of
 805 1:50, $L = 0.1$ at a 1:10 liquor ratio and $L = 0.2$ at a liquor ratio of 1:5) then a value of $[D]_s$ of say, 10,
 806 secured using a 1:5 liquor ratio can be expected to increase to 100 if a liquor ratio of 1:10 was
 807 employed. From this simple example, it follows that it is the effect of liquor ratio on the amount of
 808 dye in solution that will influence the final partition of the dye between the fibre and solution phases.

809

810 This is further reflected in terms of the marked influence which the solubility of the dye in the
 811 dyebath has upon the substantivity coefficient, S , of the dye, because of the term $([D] - [D]_s/L / [D]_s/L)$
 812 in Eq 12, according to which, the substantivity of the dye (ie S) will increase with decreasing liquor
 813 ratio (ie increasing values of L), as is observed in practice, because the amount of dye in solution,
 814 $[D]_s$, decreases with decreasing liquor ratio owing to the relationship $([D]_s/L)$; hence, the partition of
 815 the dye will shift towards the fibre phase, $[D]_f$. The predictions inherent in Eq 12 that $[D]_s$ increases
 816 with increasing liquor ratio, accords with practical observation, as depicted in the relationships
 817 described in Figure 6, between the numerical value of L and the amount of water in the dyebath as
 818 a function of liquor ratio.

819

820 The similarity between Eq 12 and Eq 8 is evident and, therefore, the arguments previously
 821 recounted in section 5.1.1 can be used to show that the observed promotion of direct dye uptake

822 onto cellulosic fibres imparted by lowering the liquor ratio employed for dyeing can be explained in
823 terms of the combined effects which increased dye aggregation and reduced dye solubility have
824 upon the substantivity coefficient, S , of the dye.

825

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

833

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

837

838 4.3.3 comparison of the two equations

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

850 exhausted dyebath at the end of dyeing. Both models suggest that direct dyeing should be
851 achievable in the complete absence of added inorganic electrolyte using low liquor ratios.

852

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

859

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

863

864 5 analysis of published data

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

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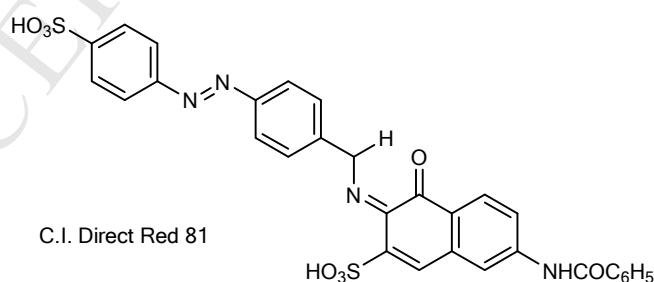
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874 In this particular study (15), Bird *et al* applied purified C.I. Direct Red 81 to a union of cotton and
875 wool fabrics employing five liquor ratios (1:20, 1:40; 1:60; 1:80 and 1:100) and varying amounts of
876 added Na_2SO_4 , ranging from 10%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



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

879

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

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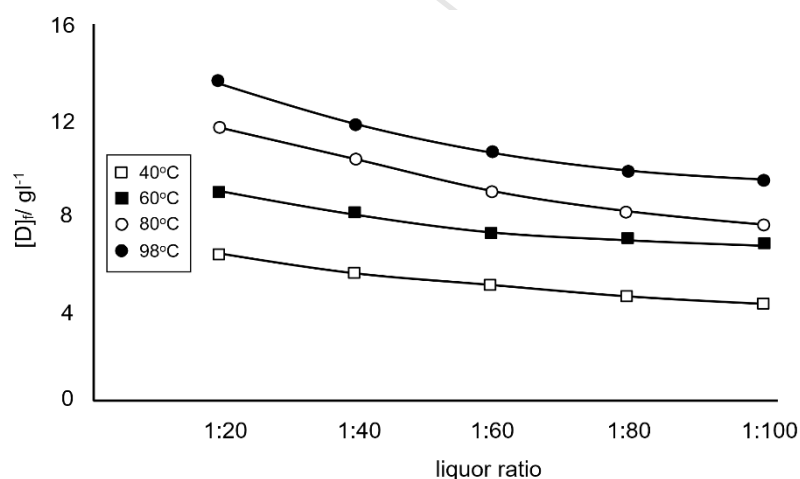
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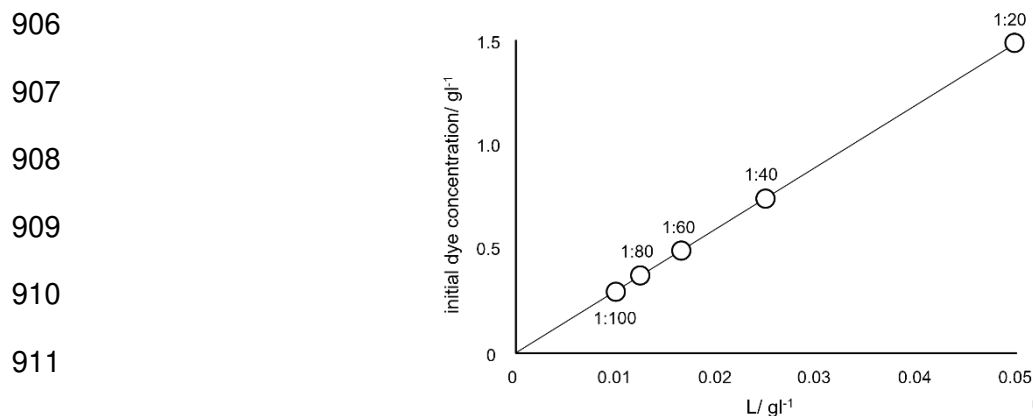
899 Figure 9 Effect of liquor ratio on uptake of purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1} Na_2SO_4 ; plotted using
 900 data from (15)

901

902 In this context, as Bird *et al* (15) applied a 3% omf depth of shade, then in going from a 1:100 to a
 903 1:20 liquor ratio, the concentration of C.I. Direct Red 81 in the dyebath at the start of dyeing would



904 increase by a factor of five, based on liquor volume (ie 0.3 g l^{-1} @ 1:100; 0.375 g l^{-1} @ 1:80; 0.5 g l^{-1}
 905 @ 1:60; 0.75 g l^{-1} @ 1:40; 1.5 g l^{-1} @ 1:20).



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

914

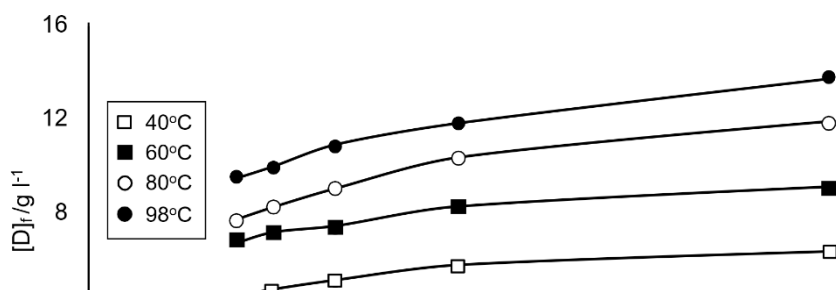
915 When these values of initial dye concentration are plotted as a function of fractional liquor ratio, an
 916 essentially linear relationship is obtained (Figure 10; the various liquor ratios that correspond to the
 917 values of L are displayed in the figure). Thus, if increased diffusional dye transfer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

922

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

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938 Figure 11 Effect of initial dyebath concentration on uptake of purified C.I. Direct Red 81;

939 3% omf dye; $5 \text{ g l}^{-1} \text{ Na}_2\text{SO}_4$; plotted using data from (15)

940

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

945

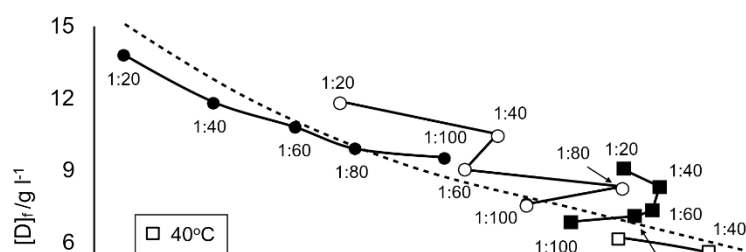
946 The results obtained by Bird *et al* (15) can be interpreted using Eq 12 since, as mentioned, this
 947 equation describes the partition of the dye between the dyebath, *s* and fibre, *f*, phases in terms of
 948 the substantivity coefficient, *S*, secured at the end of the immersion dyeing process.

949

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

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

969

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

975

976 Thus, the data displayed in Figure 12 show that the contribution of $[D]_s/L$ was greater than that of
 977 $[D]_f$ in terms of the observed reduction in partition coefficient imparted by a decrease in liquor ratio,
 978 although the contribution of $[D]_s/L$ diminished as dyeing temperature increased. These results imply
 979 that it was the amount of dye present in the dyebath, $[D]_s$, which determined the amount of dye
 980 adsorbed by the fibre, $[D]_f$, and, thereby, the partition of the dye between the dyebath and fibre
 981 phases.

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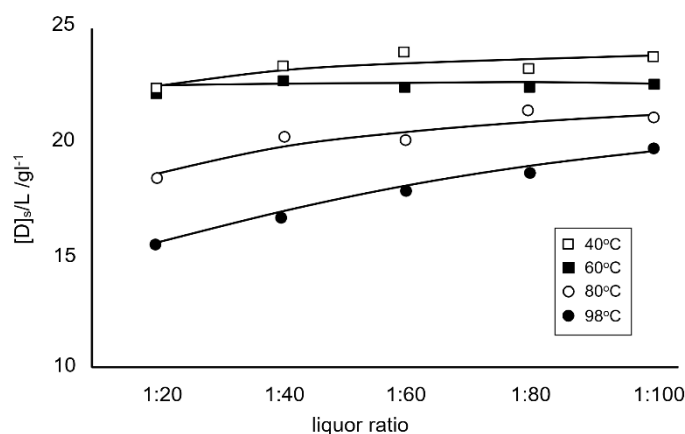
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990 Figure 13 Effect of liquor ratio on dye concentration in solution; purified C.I. Direct Red 81;

991 3% omf dye; 5 gl^{-1} Na_2SO_4 ; plotted using data from (15)

992

993 Support for this proposal accrues from the findings in Figure 13 that the concentration of dye in

994 solution (ie the dyebath), $[D]_s/L$, increased with increasing liquor ratio. From the foregoing

995 discussion, this can be attributed to there being more water available for the given amount of dye to

996 dissolve. The observation that the contribution of $[D]_s/L$ diminished as dyeing temperature increased997 is reflected in the plots shown in Figure 13 which show that values of $[D]_s/L$ decreased with998 increasing dyeing temperature (ie followed the order: $40^\circ\text{C} > 60^\circ\text{C} > 80^\circ\text{C} > 98^\circ\text{C}$), for each of the

999 five liquor ratios used. However, this finding contrasts to that observed for the effect of dyeing

1000 temperature on values of $[D]_f$ (Figure 9), which were found to increase with increasing dyeing1001 temperature, (ie followed the order: $98^\circ\text{C} > 80^\circ\text{C} > 60^\circ\text{C} > 40^\circ\text{C}$) for each of the five liquor ratios

1002 used. This can be explained by assuming that as dyeing temperature increases, more dye will

1003 dissolve in solution and, therefore, more dye will be available for dye uptake. Also, both the rate and

1004 extent of dye diffusion within the fibre can be expected to increase with increasing dyeing

1005 temperature. Thus, since $[D]_s/L$ increases with increasing dyeing temperature then so too will $[D]_f$.

1006

1007 Since Bird *et al* (15) employed added electrolyte (Na_2SO_4) to apply the disulphonated C.I. Direct

1008 Red 81, the effect of liquor ratio on the concentration of electrolyte in the dyebath at the start of

1009 dyeing warrants discussion. In early work concerned with the classification of the dyeing behaviour

1010 of direct dyes, Lemin *et al* (7) observed considerable divergence between the dyeing performance

1011 of a range of commercial direct dyes at two different liquor ratios (1:5 and 1:60) and concluded that

1012 the most important contribution to this observed effect was the electrolyte content of the commercial

1013 dyes used. Commercial dyes contain various additives (anti-dusting agents, buffers, antifoams,

1014 etc.), including neutral electrolytes such as Na_2SO_4 and/or NaCl that are incorporated into the

1015 commercial dye powder, liquid, etc (5) as part of the process that is used to obtain commercial dye

1016 products (powders, liquids, etc.) of the desired tinctorial strength. The nature and amount of the
1017 particular formulation additive used, varies, according to aspects such as the type of dye, intended
1018 dyeing method, etc. In the case of direct dyes, as neutral electrolyte is likely to be present in
1019 commercial dye samples, such additive will be present in the dyebath during dyeing. Lemin *et al*
1020 determined that the electrolyte present in commercial dye samples would impart a much greater
1021 promotion of dye exhaustion when low liquor ratios were used for dyeing than when large liquor
1022 ratios were employed for dyeing (7). Since the liquor ratio that Bird *et al* used varied from 1:100 to
1023 1:20 then so too would the concentration of additive electrolyte in the dyebath. To avoid this, Bird *et*
1024 *al* (15) used a purified (ie additive-free) sample of C.I. Direct Red 81 in their study.

1025
1026 According to the SDC classification system for direct dyes (18), some direct dyes which can be
1027 controlled by electrolyte addition alone at higher liquor ratios may require additional temperature
1028 control when applied using lower liquor ratios. Furthermore, when the amount of electrolyte utilised
1029 in dyeing is expressed as % omf rather than mass per volume, such as gl^{-1} , then a given amount of
1030 added electrolyte will impart a greater influence on dye exhaustion as liquor ratio decreases. To
1031 address these issues, the amounts of added Na_2SO_4 used by Bird *et al* (15) (ie 10%, 20%, 30%,
1032 40% and 50% omf) were such that a constant concentration of added electrolyte (5 gl^{-1}) was present
1033 in the dyebath, despite the fact that the liquor ratio varied from 1:20, 1:40, 1:60, 1:80 and 1:100.
1034 Thus, in the data collected by Bird *et al* (59), even though the effective dye concentration in the
1035 dyebath at the start of dyeing increased by a factor of five based on liquor volume (as the amount of
1036 dye used was calculated on the basis of % omf), in going from a 1:100 to a 1:20 liquor ratio, the
1037 effective concentration of added electrolyte in the dyebath was the same irrespective of liquor ratio.
1038 Hence, the observed increase in dye uptake that accompanied a decrease in liquor ratio (Figure 9)
1039 cannot be attributed to an increase in electrolyte concentration in the dyebath and, therefore, the
1040 promotional effect of reduced liquor ratio on dye uptake can be assumed to relate to a characteristic
1041 of the dye alone.

1042

1043 To expand upon this proposal, brief excursions into dye aggregation in solution, fibre swelling and
1044 dye diffusion in the fibre seem appropriate.

1045

1046 As mentioned, characteristically, direct dyes are long, planar molecules solubilised by sulfonic acid/
1047 sulfonate groups, as exemplified by the three dyes used in this work, and exhibit a pronounced
1048 tendency to aggregate in aqueous solution. Such aggregation, which is exacerbated by added
1049 inorganic electrolyte, generally decreases with increasing temperature and decreasing dye
1050 concentration. In the context of the results presented in Figures 12 and 13, at a 1:20 liquor ratio, C.I.
1051 Direct Red 81 will be more aggregated than at a 1:100 liquor ratio and, therefore, because
1052 aggregation reduces with decreasing dye concentration, the solubility of the dye in the dyebath will
1053 increase with increasing liquor ratio (ie values of $[D]_d/L$ will increase with increasing liquor ratio in
1054 accordance with Eq 12, as previously discussed). This relationship was indeed secured by Bird *et al*
1055 (15) and is shown in Figures 12 and 13, insofar as values of $[D]_d/L$ increased as liquor ratio
1056 increased over the range 1:20 to 1:100, for each of the four dyeing temperatures used. As
1057 aggregation generally decreases with increasing temperature (5), it follows that at 40°C, dye
1058 aggregation in the dyebath will be greater than when dyeing had been carried out at 98°C and,
1059 therefore, $[D]_d/L$ will increase as dyeing temperature increases. Thus, at higher dyeing
1060 temperatures, the amount of dye in the dyebath available for adsorption by the fibre will be higher
1061 than at lower temperatures.

1062

1063 In addition, at higher temperatures, it is likely that fibre swelling will also be greater than at lower
1064 dyeing temperatures, as also will be both the rate and extent of dye diffusion within the fibre (5). As
1065 dye aggregation in the dyebath will decrease with increasing dyeing temperature then the amount of
1066 dye in the dyebath will be higher, enabling more dye to diffuse within the more swollen fibre. As a
1067 corollary, it follows that as dyeing temperature increased from 40°C to 98°C (Figures 12 and 13), the
1068 amount of C.I. Direct Red 81 adsorbed by the substrate $[D]_f$ increased but the amount of dye
1069 remaining in the dyebath, $[D]_d/L$, decreased, as demonstrated by the results displayed in Figures 12
1070 and 13. Indeed, as mentioned, the dotted line in Figure 12 depicts the overall effect of temperature

1071 on the partition coefficient of the dye. The slope of the dotted line reveals that at a high dyeing
 1072 temperature (98°C) values of $[D]_f$ and $[D]_s/L$ are similar whereas at a low temperature (40°C) values
 1073 of $[D]_f$ are much lower than those of $[D]_s/L$. Thus, $[D]_s$ is the dominant factor in determining the extent
 1074 of uptake by the fibre and, therefore, the partition of the dye between the dyebath and fibre phases.

1075

1076 In this context, Figure 14 shows the variation of substantivity coefficient, S , calculated using Eq 12,
 1077 as a function of liquor ratio achieved for purified C.I. Direct Red 81 on CV. It is apparent that the
 1078 slope of the curved lines obtained at each dyeing temperature increased with increasing
 1079 temperature, which can be attributed to a corresponding increase in fibre swelling and dye diffusion
 1080 within the fibre, as well as a reduction of dye aggregation within the dyebath.

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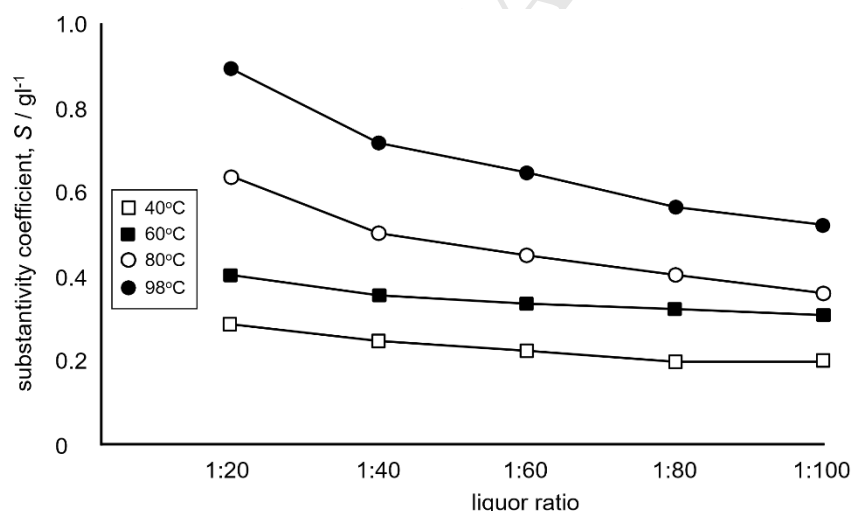
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1091 Figure 14 Effect of liquor ratio on substantivity coefficient of purified C.I. Direct Red 81; 3% omf dye; 5 gl^{-1}
 1092 Na_2SO_4 ; plotted using data from (15)

1093

1094 As the latter aspect may well be the major contributing factor, it seems appropriate to consider the
 1095 possible influence of dye aggregation in the dyebath on dye uptake. For this, the plots of $[D]_f$ as a
 1096 function of $[D]_s/L$ shown in Figure 12 will be examined. From Eq 12 it is evident that the four curves
 1097 displayed in Figure 12 describe the corresponding substantivity coefficient, S values (ie $S = [D]_f /$
 1098 $[D]_s/L$) obtained when dyeing had been carried out the four different dyeing temperatures. It is

1099 apparent that the S values obtained when dyeing had been carried out at 98°C decrease, almost
 1100 linearly with increasing liquor ratio. In the case of dyeing at 80°C, the S values take the form of an
 1101 'S' shape; however, when dyeing had been undertaken at 60°C and, especially, at 40°C, v-shaped
 1102 curves were secured. These findings can be attributed to the well-known fact that increasing
 1103 temperature reduces the extent of dye aggregation in solution (5) insofar as the marked dye
 1104 aggregation that is likely to occur at 40°C and 60°C will be much less pronounced at the higher
 1105 dyeing temperatures employed (ie 80°C and especially 98°C). Indeed, the linearity of the S values
 1106 obtained at 98°C (Figure 12) suggests that the direct dye is little aggregated in solution whilst the v-
 1107 shaped curve obtained at 40°C is indicative of extensive aggregation. In such a situation, it follows
 1108 that the slope of the curved lines shown in Figure 12 increase with increasing dyeing temperature
 1109 because of a corresponding reduction in the extent of aggregation in solution.

1110

1111 In this context, as discussed above, according to the model of direct dye uptake described by Eq 12,
 1112 the inherently low substantivity displayed by the dyes towards cellulosic fibres in the absence of
 1113 added electrolyte is attributable to the dye's marked preference for the aqueous dyebath phase,
 1114 which stems from the dye's high aqueous solubility. Reducing the liquor ratio used for dyeing
 1115 encourages dye aggregation which reduces the solubility of the dye in the dyebath phase, so that
 1116 the intrinsic preference of the previously highly soluble dye to favour the aqueous phase shifts
 1117 towards the fibre phase and so dye uptake is promoted. Thus, it follows that the substantivity of the
 1118 dye, as expressed by the substantivity coefficient, should decrease with increasing liquor ratio, at
 1119 each of the four dyeing temperatures employed, as indeed was found to be the case (Figure 15).

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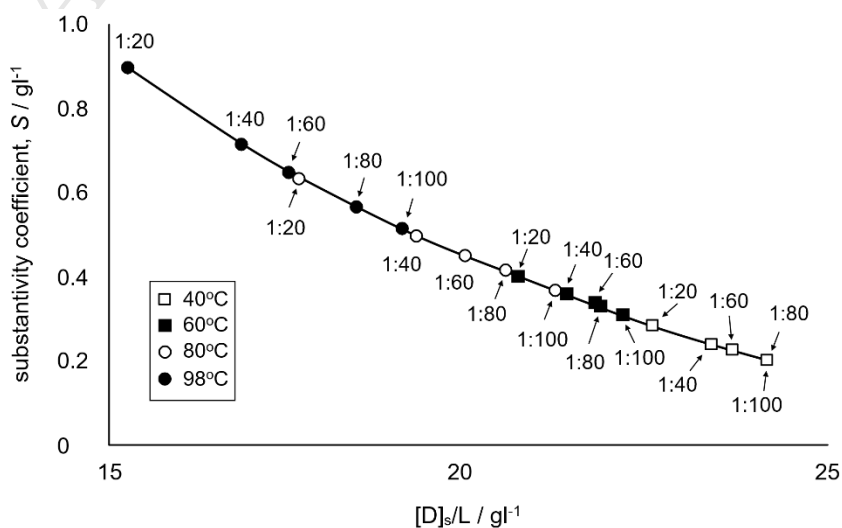
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1130 Figure 15 variation of substantivity coefficient as a function of $[D]_s/L$; purified C.I. Direct Red 81; 3% omf dye; 5
 1131 gl^{-1} Na_2SO_4 ; plotted using data from (15)

1132

1133 Interestingly, the variation of S as a function of $[D]_s/L$ depicted in Figure 15 bears a close
 1134 resemblance to the variation of $[D]_f$ as a function of $[D]_s/L$ shown in Figure 12, insofar as both plots
 1135 have negative slopes and the arrangement of the individual data points relating to the particular
 1136 liquor ratio used, as shown by the coincidence of variation of the substantivity coefficient, S , and
 1137 $[D]_f$, as a function of $[D]_s/L$ in Figure 16. Indeed, the curvilinear plots secured for the variation of both
 1138 S and $[D]_f$ as a function of $[D]_s/L$ depicted in Figure 16 are not too distant cousins, which implies that
 1139 Eq 12 (ie $S = ([D] - [D]_s/L) / [D]_s/L$) appears to provide a reasonable fit to the experimentally observed
 1140 variation of $[D]_f$ as a function of liquor ratio. In turn, this suggests that the assumptions inherent in
 1141 Eq 12 namely that reducing the liquor ratio used for dyeing reduces the solubility of the dye in the
 1142 bulk dyebath phase, because of increased dye aggregation, so that the inherent preference of the
 1143 dye to favour the aqueous phase shifts towards the fibre phase.

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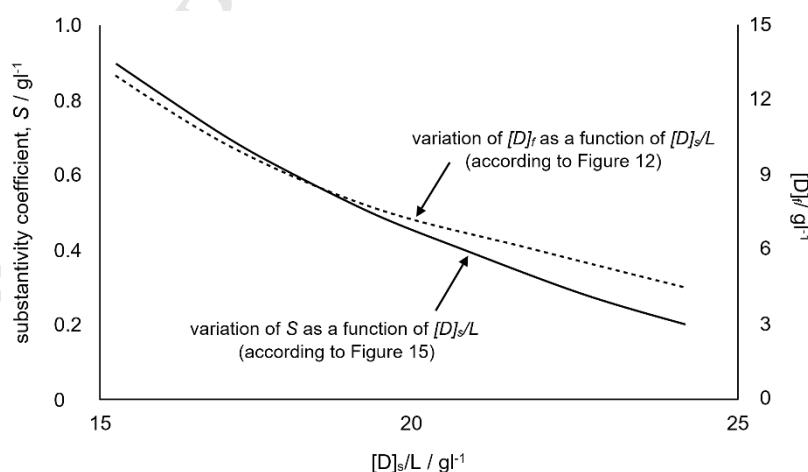


Figure 16 coincidence of variation of substantivity coefficient, S , and of $[D]_f$, as a function of $[D]_s/L$

6 conclusions

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

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

Two equations were derived to interpret the theoretical model of direct dye. Each equation invoked the concept of interstitial water in dyeing, but differed in terms of both the particular stages of the immersion dyeing process to which they apply and the type of data that is required for their solution.

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

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

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

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