Interaction of vinylsulphone reactive dyes with cellulosic fabrics. Part 1 – dyeing mechanism, fibre characterisation and effects of alkaline electrolytes

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Two vinylsulphone dyes were studied by an HPLC technique under alkaline conditions in order to evaluate their various chemical forms. Fabrics made from viscose fibres were dyed under controlled conditions, varying the nature and the quantity of electrolyte used. It was found that sodium chloride is the most efficient salt for a short dyeing times (20 min) while lithium chloride yields higher dye uptake over more prolonged dyeing processes (60 min). The effect of the electrolytes on dye uptake was found to be related to the radius of the solvated cation.

INTRODUCTION

The molecule of a reactive dye contains one or more reactive groups capable of forming a covalent bond with a compatible fibre group. The main steps in the dyeing procedure with a dye of this type comprise adsorption on the fibre, diffusion into the fibre and reaction with the specific groups of the fibre (such as hydroxy groups of cellulose or amino groups of wool) [1]. The quality of dyeing (colour and fastness) is related to the quantity of dye chemically fixed to the fibre. During the dyeing process the fabrics are generally in an alkaline environment [2], and electrolytes tend to reduce considerably the charge on the fibre [3–5], thus facilitating the transfer of dye from solution into the fibre.

In this paper we are interested in reactive dyes of the vinylsulphone type. In fact, the vinylsulphone group is

not normally present in the stable form of the dyes, and it is necessary to use a precursor such as β-sulphatoethylsulphone, which increases the stability and the solubility of the dye. Examples of such dyes are the Remazol range from Hoechst. In the presence of alkali the β-sulphatoethylsulphone group is converted into the vinylsulphone group, the formation of this last compound being necessary for reaction with cellulose [6–8] to give compound A (Figure 1). The following points were investigated:

(a) Transformation of the various chemical forms of two vinylsulphone dyes in the dyeing process
(b) Influence of a series of electrolytes (nature and amount) upon the dye uptake by cellulose.

$D-SO_2-CH_2-CH_2-O-SO_3Na$	β-Sulphatonethylsulphone
$D-SO_2-CH=CH_2$	Vinylsulphone
$D-SO_2-CH_2-CH_2-O-cell$	A

where D = chromophore
cell-OH = cellulose

Figure 1 Different forms of vinylsulphone dye species

EXPERIMENTAL

Materials

Desized, scoured and bleached viscose fabrics of 96 g/m^2 weight were supplied by DMC (Ecully, France). The fabric samples were woven from continuous-filament viscose yarns; the number of matt warp threads (110 dtex) was 48 per cm and the weft threads 28 per cm. Remazol Red F3B (CI Reactive Red 180) and Remazol Yellow GNL (CI Reactive Yellow 23) (Figure 2) were the dyes used in this work. The following electrolytes (Prolabo) were selected in order to assess their effectiveness in promoting dye uptake: lithium, sodium, potassium and caesium chlorides, and sodium sulphate.

Apparatus

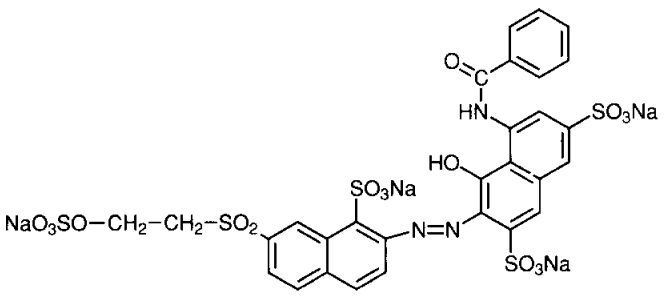
Spectra of solutions were recorded on a Varian 634 spectrophotometer at room temperature. Solutions with dye concentration around 10^{-4} mol/l were examined in Hellma cells with a 10 mm path length. Reflectance measurements were performed on an ACS Colorquest spectrophotometer. The pH values were measured on a Tacussel Isis 20000 potentiometer.

The high-performance liquid chromatography (HPLC) system was used consisting of a Spectra Physic (Isochrom 020) pump, a Valco model C6W liquid chromatograph injector (20 µl injected), a Hypersil C-8 reverse-phase analytical column (25 cm × 4.6 mm internal diameter) and a Lirec UV 904 absorbance detector with a fixed wavelength at 254 nm. The eluant composition was 50% aqueous 0.005 mol/l tetrabutylammonium chloride and 50% acetonitrile.

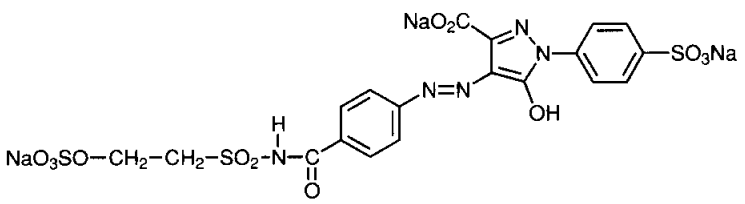
The viscose samples were dyed using an Ahiba Texomat G7B apparatus.

Dye purification

The commercial dyes used in this work are blended with sodium sulphate to adjust the dyeing strength to a constant value guaranteed by the manufacturer. For convenient chemical investigations it is necessary to purify the dye by means of successive crystallisations. This was done by dissolving 10 g samples of vinylsulphone dye in 10 ml dimethylsulphoxide at 60°C. Sodium sulphate was eliminated by filtration, and the dyes were precipitated in 500 ml n-butanol at room temperature over 15 min. The dyes were filtered and washed twice with ethanol, then with ethyl ether. The purified dyes were dried at 60°C. All sequences were repeated twice [9–11].



Remazol Red F3B



Remazol Yellow GNL

Figure 2 Chemical structures of the dyes Remazol Red F3B and Remazol Yellow GNL

The purity was checked colorimetrically until the absorbance and the absorption maxima in a standard solution remained unchanged (Table 1). Based on the concentration by weight of the initial solution, the molar absorption coefficients ε allow estimation of the amount of impurities (mainly sodium sulphate) present, about 18% for Remazol Red F3B and about 29% for Remazol Yellow GNL.

Table 1 Colorimetric characterisation of dyes used in the present study

	ε (l/(mol cm))			
Remazol	Before purification	First purification	Second purification	λ_{max} (nm)
Red F3B	18 889	26 730	26 730	540/510
Yellow GNL	17 179	21 025	21 025	430

Dyeing process

Dyeings were performed by raising the temperature to 50°C and dyeing for 20 min. The initial pH of the bath was 11.5, which decreased to 11.3 during dyeing. In each dyeing 2 g viscose samples were used and the dye concentration was 10^{-4} mol/l. A sodium carbonate/sodium phosphate (5 g/l of each) buffer was used, together with sodium chloride (100 g/l). The liquor ratio was 25:1 and the bath volume 50 ml.

Dye liquor, buffer liquor and fabrics were mixed together at the outset, and the fabrics agitated in the dyeing apparatus. At the desired time the viscose sample was transferred from the dyeing tube to a washing tube containing 60 ml aqueous solution (2 g/l) of a commercial detergent. The temperature was raised to 60°C and the sample washed for 15 min, with agitation. The sample was then rinsed twice with 50 ml distilled water, dried and ironed before carrying out reflectance measurements.

The residual dyebath was added to the washing bath and rinsing solutions. After adequate dilution the concentration of dye was determined by colorimetry.

Determination of dye uptake

Visible spectroscopy is the most commonly used technique for quantitative determination of dye concentration, either in the dyebath or on the fibre. Measurements can be performed by absorbance spectrophotometry of dye solutions or by reflectance spectroscopy.

Solution absorbance measurements allow the quantity of the dye which disappears from the bath during the dyeing process to be assessed. The two dyes used in the present work are known to have high wash fastness values (rating 5) [12], so it was assumed that all the dye not chemically bound to the fibre was eliminated during the washing step. This assumption was corroborated by performing a washing fastness test (rating of 4–5), according to French standard NF G07-200. The dye uptake T was then defined in terms of the quotient of the dye covalently bound to the fibre and the total amount of dye initially present in the bath (Eqn 1):

$$T = \left(1 - \frac{A}{A_0}\right) \times 100 \qquad (1)$$

where A_0 represents the maximum absorbance of bath solutions before dyeing and A the maximum absorbance of combined bath solutions (after the dyeing, washing and rinsing processes).

Because of discrepancies that can occur between strength and shade evaluations in solution and on textile substrates, reflectance spectroscopy is often the preferred analytical technique. It relies on two kinds of parameter:

(a) A characteristic parameter of the dyeing process, generally based on the Kubelka–Munk relationship between spectral reflectance R, the Kubelka–Munk spectral absorption constant K and the spectral scattering constant S [13] (Eqn 2):

$$K/S = \frac{(1 - R)^2}{2R} \qquad (2)$$

In practice, the relationship between dye concentration and K/S value is not completely linear and measurements are repeated for reliable averages.

(b) A relative parameter based on formulae which transform the visually non-uniform tristimulus colour space into a visually uniform space. In this study the CIELAB formula was used [13]. This allows splitting of the total colour difference ΔE^* into three parts: lightness difference ΔL^*, hue difference ΔH^* and chroma difference ΔC^*.

RESULTS AND DISCUSSION

Stability in alkaline medium

During dyeing in an alkaline medium, chemical modifications of the reactive group of the dye take place, so a knowledge of the behaviour of the reactive precursor is useful for a thorough understanding of the properties of vinylsulphone dyes.

The aqueous solubility of commercial reactive dyes in the β-sulphatoethylsulphone form generally varies according to the number of sulphate ester groups present. Treatment by alkali results in formation of vinylsulphone by deprotonation and sulphate elimination. Further reaction at 90–100°C and pH values above 11.5 with hydroxy or carboxylate ions leads to hydroxyethylsulphone and occasionally ether [2,7,14,15]. The formation of vinylsulphone can be followed very easily by measuring the pH of concentrated dye solutions during the addition of alkali.

$$D{-}SO_2{-}CH_2{-}CH_2{-}OSO_3^- + OH^- \longrightarrow D{-}SO_2{-}CH{=}CH_2 + H_2O + SO_4^{2-}$$

$$D{-}SO_2{-}CH{=}CH_2 + H_2O \xrightarrow{OH^-} D{-}SO_2{-}CH_2{-}CH_2{-}OH$$

$$D{-}SO_2{-}CH_2{-}CH_2{-}OH + D{-}SO_2{-}CH{=}CH_2 \longrightarrow (D{-}SO_2{-}CH_2{-}CH_2)_2O$$

Scheme 1

In the presence of alkali, during the dyeing process, the four chemical forms can exist in the bath (Scheme 1). Only the vinylsulphone form is able to react chemically with the hydroxy groups of cellulose. Other forms not reacting with cellulose can be eliminated gradually during successive washings.

In order to monitor the vinylsulphone concentration in the dyebath, many HPLC procedures have been developed for the separation and quantification of dyes, and in particular ion-pair chromatography (IPC) procedures [10,16]. In IPC processes tetrabutylammonium ions, as counterions for anionic dyes, are included in the mobile phase to form ion pairs with the components and thus allow the elution of the dyes [17]. In the present work we sought to determine the optimum time of dyeing, which is closely dependent on the actual vinylsulphone concentration.

Thus 45 ml buffer solution (sodium carbonate + trisodium phosphate, pH 11.5) were heated in a dye tube at 50°C. At the beginning of the experiment 5 ml dye solution (12 g/l) were added and the mixture stirred. The concentration of dye in this solution became similar to that in the experimental dyeing bath (1.2 g/l). Every 5 min a portion of the solution was withdrawn, neutralised and analysed by HPLC, which revealed the concentrations of the various dye species present. The pH value was 10.6 after 60 min. Figure 3 shows that the vinylsulphone concentration decreased rapidly during the first 30 min, and the hydroxyethylsulphone concentration increased accordingly. The concentration of the ether form remained approximately constant at about 5–10%.

It was interesting to observe that Yellow GNL reached 50% hydrolysis (half life) in 7 min, but Red F3B required 15 min for this to occur. Yellow GNL can also react more rapidly with the cellulose fibre by the same mechanism.

Characterisation of the fibre

The cellulose in viscose fibres consists of β-D-glucopyranose units (Figure 4), but with a lower degree of polymerisation than cotton cellulose. Three hydroxy groups per glucopyranose unit are theoretically reactive towards vinylsulphone dyes. In practice, only a small portion of them actually react, hydroxy groups located in crystalline regions being inaccessible.

Cellulosic fibres react at pH 9–12. In the presence of dyes the relative reactivities of the hydroxy groups are not precisely known, but it has been demonstrated that positions 2 and 6 of the glucopyranose unit are the most probable reaction sites [6,18]. Furthermore, the chain-end glucopyranose units are able to react with the reactive dye molecules, and these are more numerous in viscose than in cotton because of the lower degree of polymerisation.

The treatment of cellulosic fibres by various oxidising agents leads to scission of the C_2–C_3 linkage, with ultimate oxidation to carboxylic acid groups. Therefore it is easy to determine the ratio of the carboxylic acid groups by an exchange reaction with calcium acetate, and then titrating the acetic acid with alkaline solution [19]. The ratio of the carboxylic acid groups in the fabrics used in this study were found to be 0.27, which was in accordance with usual values for such viscose samples.

The degree of polymerisation was determined by viscosimetric measurements according to the French

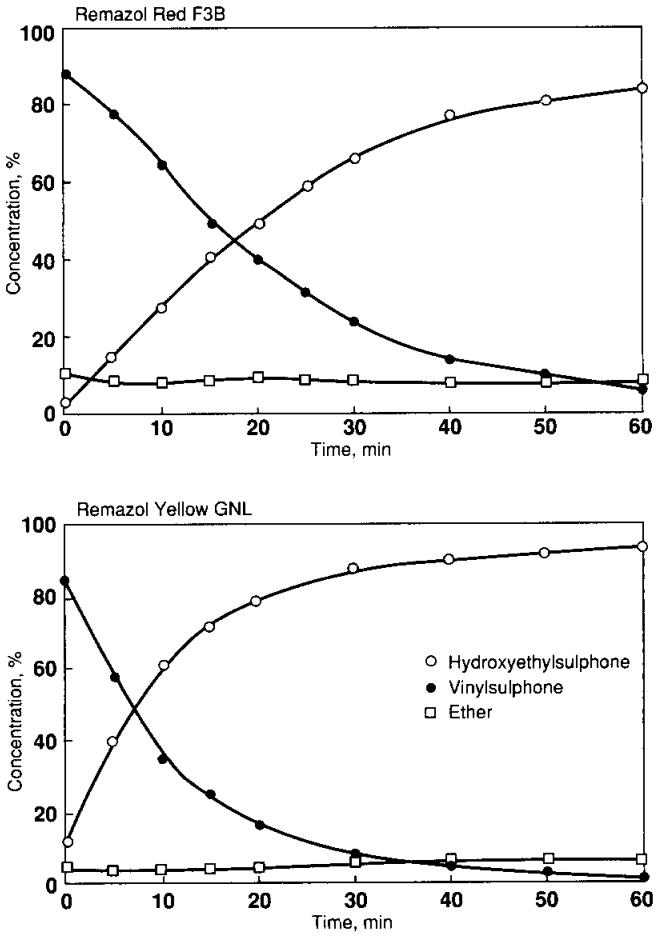


Figure 3 Transformation of Remazol Red F3B and Remazol Yellow GNL vinylsulphone dyes at 50°C and pH 11.5

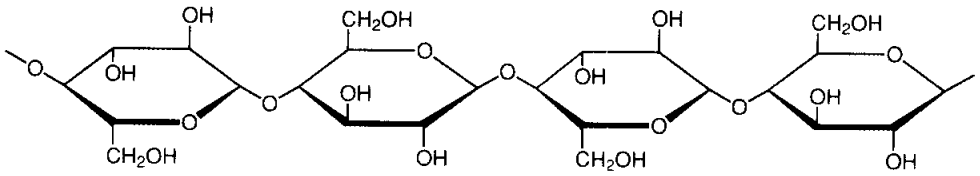


Figure 4 Structure of cellulose

standard G06-037 relating to cellulosic textiles (similar to international standard ISO/DIS 5351/1). The method consists of measuring the specific viscosity of a cellulosic sample in a dilute solution of a cupriethylenediamine complex. The average value obtained for the degree of polymerisation (DP) was compared with values for the warp and the weft of a standard cotton sample (Table 2). The low average degree of polymerisation of the viscose sample was in good agreement with the cellulose chain length values expected for this kind of fibre [20].

Table 2 Degree of polymerisation of viscose and reference cotton sample

		Specific viscosity	C^a	Degree of polymerisation
Viscose		0.546	0.266	235
Cotton	warp	0.898	0.050	1906
	weft	0.923	0.050	1928

a Concentration in grams of dry fibre in 100 ml cupriethylenediamine complex

Effect of electrolytes

It is well known that cellulosic fibres acquire a negative charge when immersed in aqueous alkaline media because of their dielectric constant is lower than that of water [5]. Some workers have explained the effect of electrolytes on the basis of a decrease in the negative surface potential of the fibre, the relative fibre–dye potential remaining negative and involving a repulsive effect [5,21]. Sodium chloride and sodium sulphate are generally known to produce a good dyebath exhaustion, but the relatively large quantity of electrolyte needed (100 g/l) is often considered as a disadvantage from an environmental point of view.

Values of dye uptake after 20 min were determined using dyebaths that contained different amounts of electrolyte, and in every case they were calculated from colorimetric measurements. Reflectance measurements led to the same classification in terms of efficiency of the electrolytes. With most uni–univalent electrolytes the dye uptake increased with increasing electrolyte concentration, but with lithium chloride the dye uptake reached a maximum value at about 40 g/l electrolyte (Figure 5). The following general trends were observed :

(a) Without electrolyte, the dye uptake after 20 min was greater in the case of Yellow GNL, probably because its substantivity for viscose is greater than that of Red F3B

(b) At an electrolyte concentration of 100 g/l, values of T decreased in the order NaCl > KCl > CsCl > LiCl

(c) With NaCl, KCl and CsCl, dye uptake after 20 min increased progressively with concentration; the curves obtained with LiCl showed a maximum at about 40 g/l electrolyte

(d) The value of T depended more on the type and quantity of electrolyte with Red F3B than with Yellow GNL; it seems reasonable to assume that Red F3B is more sensitive to the ionic environment because it contains four negative charges per anion, compared with only three for Yellow GNL.

A series of measurements were carried out at set intervals until equilibrium was attained so that the optimum dyeing conditions could be identified (Figure 6). The effects of sodium and lithium chlorides depended closely on the dyeing time adopted. With sodium chloride the equilibrium was rapidly reached after about 20 min, and

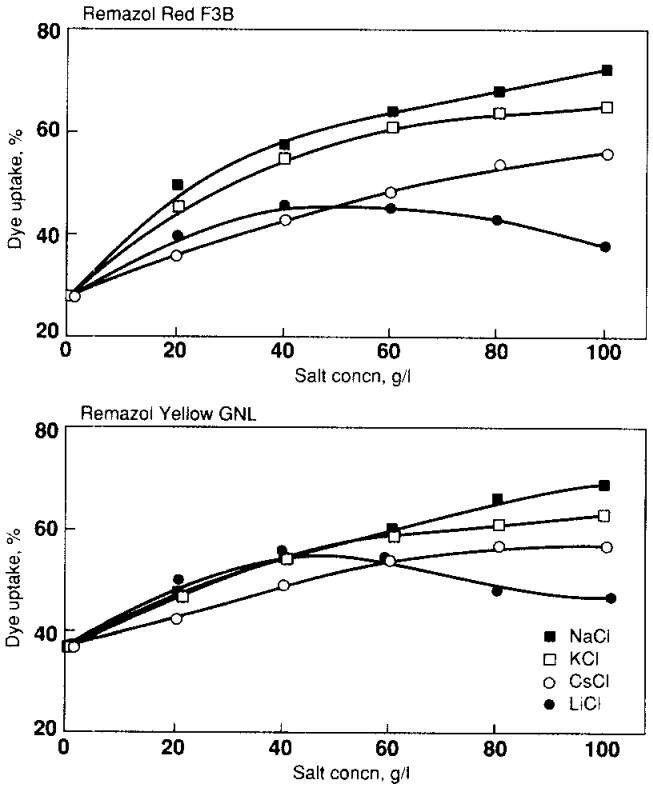


Figure 5 Dye uptake after 20 min as a function of electrolyte concentration for Remazol Red F3B and Remazol Yellow GNL

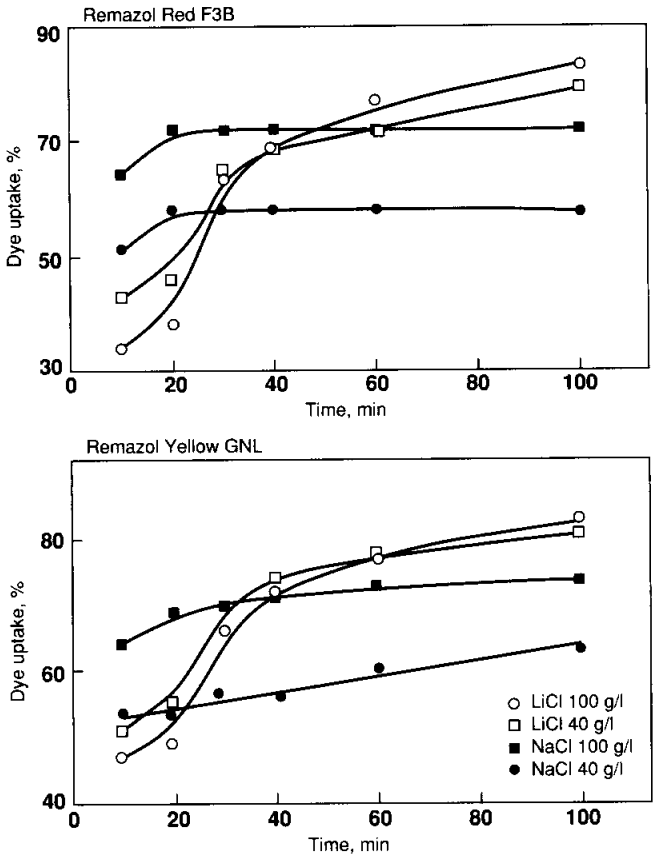


Figure 6 Dyeing rate curves for Remazol Red F3B and Remazol Yellow GNL

depended largely on the amount of electrolyte present, while with lithium chloride for the first 20 min the dye uptake was relatively low but during the next 20 min a rapid increase is observed, and from 40 min the dye uptake values were always higher than those obtained with sodium chloride. Surprisingly, at low reaction times higher values of T were obtained with 40 g/l lithium chloride. Dye uptake with 100 g/l lithium chloride became greater after 40–60 min, but equilibrium still seemed not to be reached. This phenomenon is currently under investigation.

In order to facilitate adsorption (and then reaction) on the fibre, competitively with hydrolysis of the vinylsulphone, it would seem to be advantageous to transfer the maximum amount of dye in the precursor form to the fibre prior conversion to the vinylsulphone form [16,22,23]. This two-stage process was tested using the experimental conditions adopted in the present work (20 min dyeing) with the addition of alkali delayed for 10 min. No significant effect was observed in terms of uptake for either dye.

Other salts were also tested to compare their efficiency: ammonium, calcium and magnesium chlorides; zinc diacetate; and sodium, ammonium and aluminium sulphates. Under the conditions employed (60 min controlled dyeing cycles with 100 g/l electrolyte), a negative effect on dye uptake was always observed, except with sodium sulphate.

With five of the electrolytes used (lithium, sodium, potassium and caesium chlorides, and sodium sulphate) it was decided to correlate their effect on dye uptake with ionic radius and screening constant of the cation (Table 3). When dyeing with direct dyes, it has been shown previously that alkali metal electrolytes exert an increasing effect on dye uptake as the ionic radius increases [24]. This is the opposite to what we found in the present study, in which electrolyte was directly correlated with the size of the solvated cation, rather than that of the cation alone. On the other hand, a small value of screening constant favours better neutralisation of the cellulosate anions, leading to higher adsorption of the anionic dye.

CONCLUSIONS

When dyeing with vinylsulphone reactive dyes at pH 11.5, the precursor form is rapidly transformed into the vinylsulphone form, and then into β-hydroxyethylsulphone.

At a concentration of 100 g/l electrolyte, a comparison of five alkali metal electrolytes shows two points:

(a) Sodium chloride is the most efficient salt for a short dyeing time (20 min)

Table 3 Dye uptake after 60 min as a function of ionic radius of univalent cation

Electrolyte[a]	Ionic radius (Å)		Water associated with solvated cation (mol)	Screening constant (eV)	T (%)	
	Cation	Solvated cation			Red F3B	Yellow GNL
Lithium chloride	0.78	2.30	5	1.70	77	78
Sodium chloride	0.98	1.79	4	8.50	71	73
Sodium sulphate	0.98	1.79	4	8.50	69	69
Potassium chloride	1.33	1.22	3	16.8	64	65
Caesium chloride	1.65	1.17	2	52.8	56	57

a Electrolyte concentration 100 g/l

(b) Over a complete dyeing process (equilibrium after 60 min) lithium chloride promotes a higher uptake of dye, and under these conditions the electrolyte efficiency increases with increasing radius of the solvated cation: CsCl < KCl < Na_2SO_4 < NaCl < LiCl. Dye uptake increases progressively with the increase in salt concentration, except with lithium chloride which shows a maximum uptake of dye at a concentration of 40 g/l.

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