Sorption isotherms and behaviour of direct dyes on lyocell fibres

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Abstract

Lyocell fibres, new solvent spun cellulosic polymers, have some advantages over conventional viscose fibres: less pollution produced during the manufacturing process and improved mechanical properties in particular high modulus and tenacity when wet. The aim of this work was centred, on the characterisation of the main influencing parameters in the yield of dyeing with the C.I. Direct Blue 1 dye through the study of equilibrium isotherms. In order to establish a quantitative analysis, some known dyeing sorption isotherms: Nernst, Freundlich and Langmuir, were compared to the experimental isotherm obtained. The free internal volume has been calculated for lyocell fibre. Also, the dyeing characteristic thermodynamic magnitudes were determined: standard affinity, entropy and enthalpy. This will allow for comparison between different operational parameters in order to evaluate the whole process of dyeing lyocell fibres with the dye used. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Lyocell fibres [1] are characterised by high modulus and excellent tenacity, particularly in wet conditions [2], due to their high degree of crystallinity and the amorphous orientation of their elementary fibrils [3]. Nevertheless it is a cellulosic fibre and therefore, all the theories developed for other cellulosic fibres should apply [4].

When the fibres are immersed in a bath, containing the sodium salt of a direct dye [5], Na_zD, and electrolyte NaCl, the adsorbed dye ions (D^-) are accompanied by sodium (Na^+) and chloride ions (Cl^-). The extent of which these are present is determined by the usual Donnan distribution between the internal phase of volume, V (l/kg), and the external solution and by the necessity to maintain the fibre electrically neutral.

If the concentration of dye in the internal phase (D_i), was considered to be in equilibrium with the adsorbed dye on the fibre (D_f), the Nernst, Freundlich and Langmuir equilibrium adsorption [6,7] (Eqs. (1), (2) and (3), respectively) can be used as is shown below:

- Nernst:

$$K = \frac{[Na_f]^z \cdot [D_f]}{V^{z+1} \cdot ([Na_s]^z \cdot [D_s])} \qquad (1)$$

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where K is the equilibrium constant, the "Na" term represents the sodium ion concentration on the fibre, $[Na_f]$ in mol/kg, and in the solution, $[Na_s]$ in mol/l, respectively. The D_s (mol/l) and D_f (mol/kg) terms represent the dye anion concentration in the solution and on the fibre, and the term z is the total charge on the dye anion. The V (in l/kg) term represents the volume of the internal pore solution and will vary and depend on the morphology of the fibre or polymer substrate.

- Freundlich:

$$K = \frac{[Na_f]^z \cdot [D_f]}{V^{z+1} \cdot ([Na_s]^z \cdot [D_s])^x} \qquad (2)$$

where x is the characteristic coefficient dye–fibre system, and for the C.I. Direct Blue 1 direct dyes on cellulose can be considered as being equal to one [8].

- Langmuir:

$$K = \frac{[Na_f]^z \cdot [D_f]}{V^z [Na_s]^z [D_s]([D_{sat}] - [D_f])} \qquad (3)$$

where $[D_{sat}]$ is the saturation value of the dye for the fibre, in mol/kg.

When added salt is present in the dye bath, the sodium ion concentration on the fibre must be calculated indirectly by using the two basic assumptions of Donnan [9]. When these assumptions are made, and a material balance considered, the following Eq. (4) can be derived [10]:

$$[Na_f] = [D_f] \cdot \left\{ \frac{z}{2} + \left(\frac{z^2}{4} + \frac{[Cl_s] \cdot [Na_s] \cdot V^2}{[D_f]^2} \right)^{\frac{1}{2}} \right\} \qquad (4)$$

The standard chemical potential of dyeing can be calculated with Eq. (5) and is commonly referred to as the dyeing affinity [10]:

$$\Delta\mu^\circ = RT \ln K \qquad (5)$$

where K represents the equilibrium constant shown in Eqs. (1)–(3), R is the gas constant and T is the temperature.

The standard enthalpy, ΔH°, and entropy, ΔS°, of dyeing can be calculated from Gibbs equation [Eq. (6)]:

$$\Delta\mu^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (6)$$

Plots of $\Delta\mu^\circ/T$ versus $1/T$ used to obtain ΔH° must yield straight lines as is shown by the following Eq. (7):

$$\Delta H^\circ/T = \Delta\mu^\circ/T + \Delta S^\circ \qquad (7)$$

Before making calculations using Freundlich equation, it is helpful to estimate "V" and "x". This was done by rearranging Eq. (2) into the following reciprocal form:

$$-\ln \frac{[Na_f]^z \cdot [D_f]}{V^{z+1}} = \frac{\Delta\mu^\circ}{RT} - x \ \ln([Na_s]^z[D_s]) \qquad (8)$$

A plot of $-\ln [Na_f]^z[D_f]/V^{z+1}$ versus $-\ln [Na_s]^z[D_s]$ should give a straight line where "x" represents the slope and $\Delta\mu^\circ/RT$ the intersection point with the y-axis.

In the work reported here, quantitative analyses of equilibrium isotherms of C.I. Direct Blue 1 have been done and the free internal volume for lyocell fibre has been estimated. Also, the characteristic thermodynamic magnitudes of dyeing lyocell fibres with the direct dye C.I. Direct Blue 1 have been determined.

2. Experimental

Samples of fabric made with 100% lyocell fibres (1.7 dtex), 196 g/m² (twill), supplied by Tencel Ltd, were used. To eliminate all the products added to the fibres in post-spinning treatments, the samples were washed in a bath containing 1 g/l of a non-ionic surfactant with a liquor ratio of 12/1 at 80 °C for 60 min. After repeated rinsing under distilled water, the samples were air-dried.

The dye used in this study was the C.I. Direct Blue 1 (C.I. 24410). This dye has been used in several studies of dyeing characterisation and to calculate the volume "V" of the internal phase of the fibre [4,10,11]. The chemical structure is shown

in Fig. 1. It was used its in commercial form (36.7% purity) without further purification. The salt concentration (NaCl) content of the dye was 17.8% w/w.

All dyeing processes were carried out in a Linitest laboratory machine. The absorbency values of the dye bath at each stage were measured using a Shimadzu PR-1 spectrophotometer at the wavelength of maximum absorbance, 620 nm.

A dye bath, containing an initial dye concentration of 1% o.w.f. and a salt concentration of 0.171 mol/l, was set-up and the time (t_{eq}) required to achieve equilibrium at a temperature of 120 °C was determined. The liquor to goods ratio was 40/1 with 5 g of lyocell samples. The time taken for the dye to achieve equilibrium was approximately 3 h

(Fig. 2), hence; all subsequent dyeings were carried out for eight hours to ensure the attainment of thermodynamical equilibrium.

Initial dyebath concentrations of C.I. Direct Blue 1, 0.5, 1, 2, 3, 4, 5, 8% o.w.f., were evaluated during the determination of adsorption isotherms. Chloride sodium concentrations of 0.0855 and 0.171 mol/l NaCl and temperatures of 80, 100 and 120 °C were used for the dyebaths. The other dyeing conditions where the same as indicated above.

3. Results and discussion

In Fig. 3 the results at different working conditions are represented. The increase in electrolyte
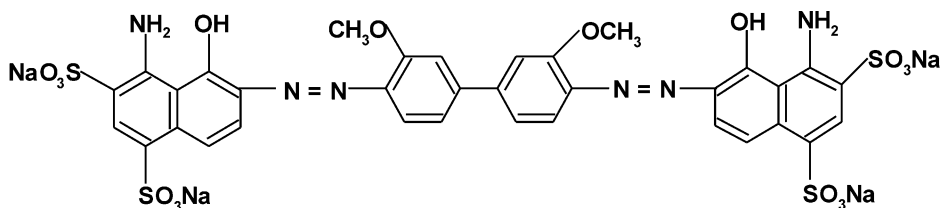
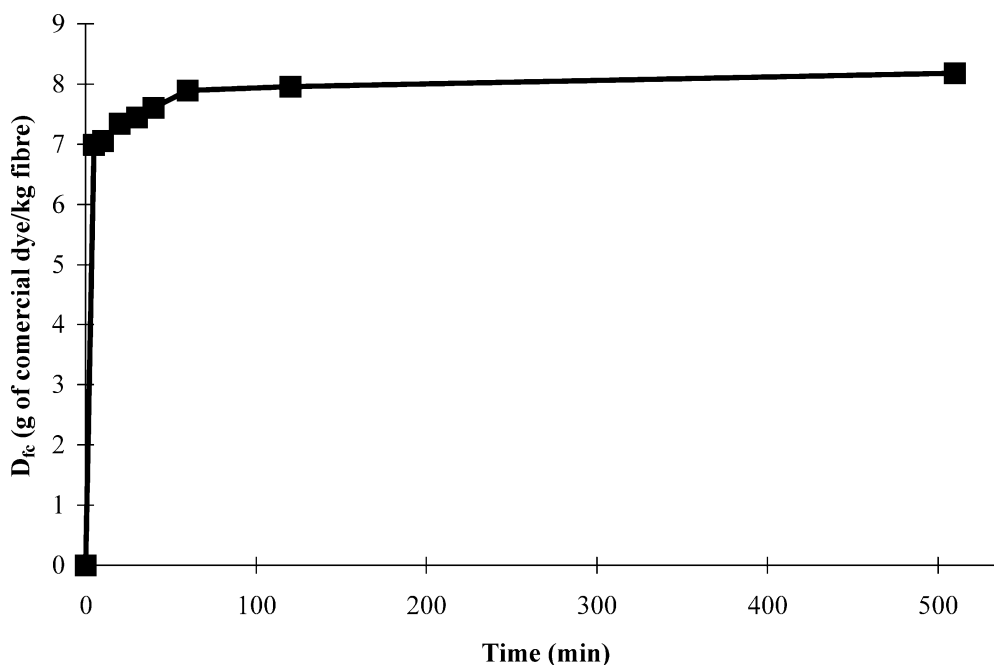

Fig. 1. Dye structure of C.I. Direct Blue 1, C.I. 24410.

Fig. 2. Dyeing equilibrium time at 120 °C and 0.171 mol/l NaCl.

concentration raises the dye adsorbed by the fibre (D_f), due to the diminishing of the electronegative potential that cellulosic fibres acquire when immersed in water solutions. The ions from the electrolyte neutralise this potential and this facilitates dye adsorption. Moreover, the osmotic work required for the accompanying Na^+ ions to be transferred is reduced.

On the other hand, the increase of temperature leads to a reduction of the dye concentration adsorbed by the fibre. As a consequence, the partition constant value ($K = D_f/D_s$) decreases, as can be deduced from the Gibbs equation [Eq. (6)]. The augment of the temperature diminishes affinity ($-\Delta\mu°$) and, therefore, the dye adsorption at equilibrium results are also reduced.

As can be observed from the results, with lyocell fibres it is necessary to use a double quantity of electrolyte when the temperature of the dyeing bath is increased by 20 °C, to obtain a similar distribution of the C.I. Direct Blue 1 dye at equilibrium.

In Fig. 4 it is shown the influence of the variables studied in the final exhaustion of the bath.

The evaluation of the isotherm models (Nerst, Freundlich, Langmuir) from the experimental results, forms the basis of the behavioural analysis of the lyocell–dye system. As is shown in Fig. 3, the plot of D_f versus D_s is not a straight line, then the Nerst isotherm fails to correlate the data. It is necessary to linearize the original Freundlich and Langmuir equations to study which equation provides a better fit with the experimental points. The correlation coefficient of the linear fit will be used as an indicator of the accuracy of the regression. The results of the Freundlich [Eq. (2)] and Langmuir [Eq. (3)] linear regression curve, at 80 °C and 0.0855 mol/l of electrolyte, are shown in Figs. 5 and 6. The remaining experimental conditions studied show the same tendency and from them it could be deduced that the best isotherm model to explain the dye adsorption of lyocell fibre is the one of Freundlich.

From the regression analysis of the Freundlich isotherm [Eq. (8) and Fig. 7], the values of $k = \Delta\mu°/RT$, the volume of the internal pore solution (V, l/kg) and the standard affinity have been calculated. Previously, it is necessary to select the values of "x" and "V" of the model because the differences between the correlation coefficients are not representative enough. Some authors have stated that for a dyeing system with a cellulose
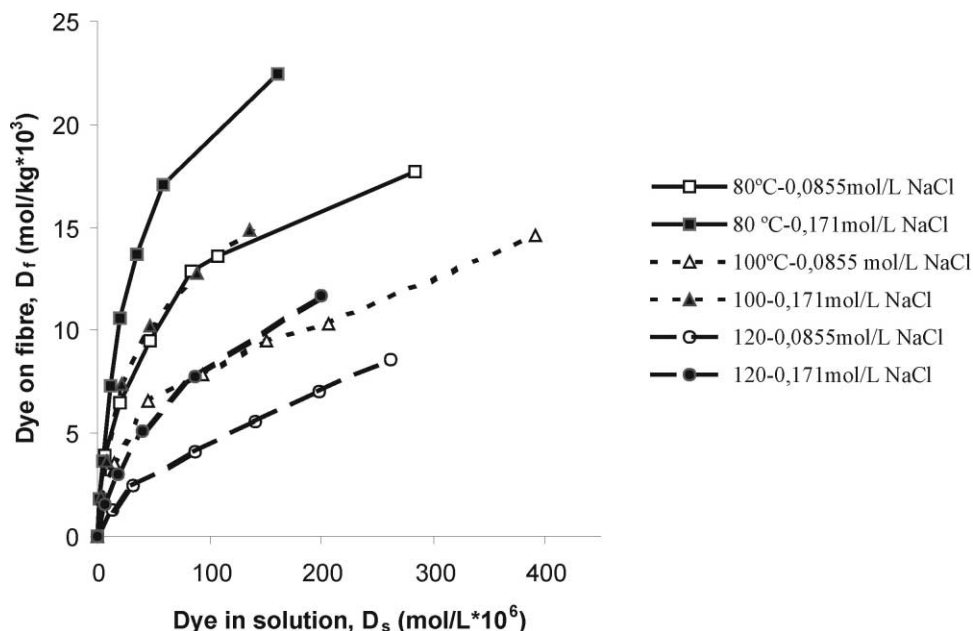

Fig. 3. Effect of temperature and electrolyte concentration on the adsorption isotherm of C.I. Direct Blue 1 on lyocell.

substrate and the C.I. Direct Blue 1, the value for "*x*" could be assumed to be equal to unity [8]. This hypothesis, previously confirmed with the experimental results, has permitted to obtain the results presented in Table 1.

If we consider the results of "*V*" obtained from the model, with 0.0855 mol/l of electrolyte concentration, and taking this as the final value of the mean, the free internal volume of lyocell fibres is found to be 0.51 l/kg. These results also confirm
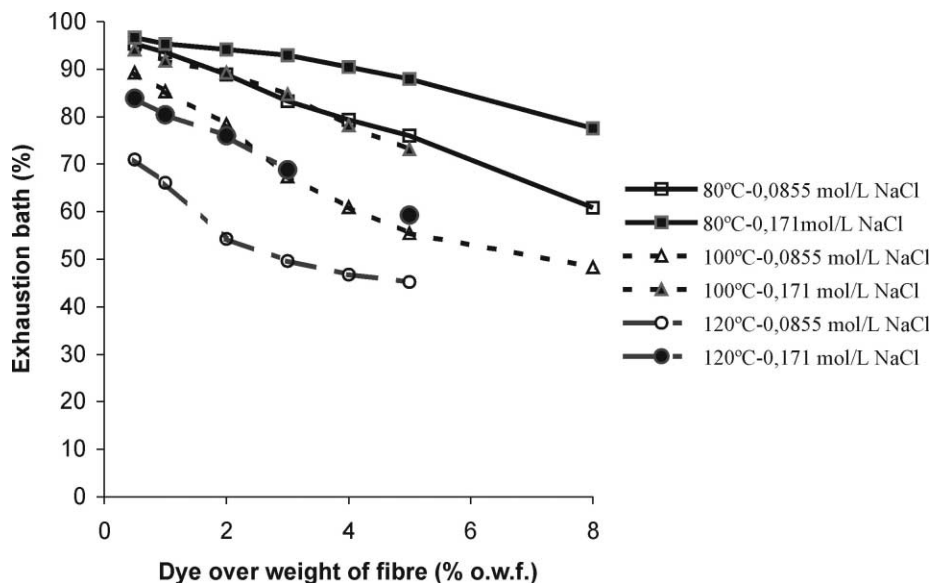

Fig. 4. Effect of initial dye concentration, temperature and electrolyte concentration on the exhaustion bath.
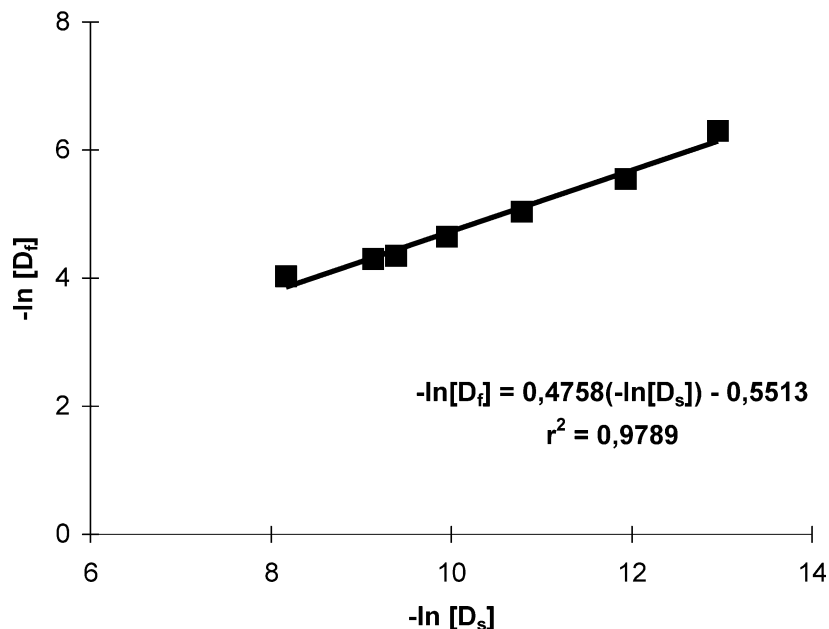

$$-\ln[D_f] = 0.4758(-\ln[D_s]) - 0.5513$$
$$r^2 = 0.9789$$

Fig. 5. Lineal regression curve of experimental results with Freundlich isotherm ($T = 80$ °C, 0.0855 mol/l NaCl).

that an increase of electrolyte concentration in the bath (0.1710 mol/l), reduces the value of "V" (mean $= 0.38$ l/kg) because there is a more intense neutralisation of the electronegative charge on the cellulose surface, modifying the electric forces in the interface, under the considerations of Donnan.

The effect of dyeing conditions on the calculated standard affinity, shows that an increase in electrolyte concentration raises the affinity, while the
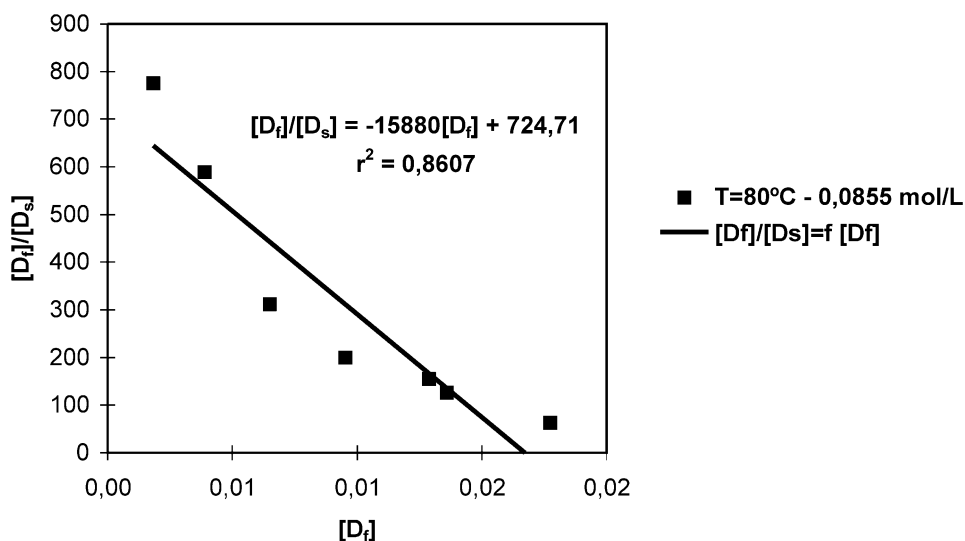

Fig. 6. Lineal regression curve of experimental results with Langmuir isotherm ($T = 80\ °C$, 0.0855 mol/l NaCl).
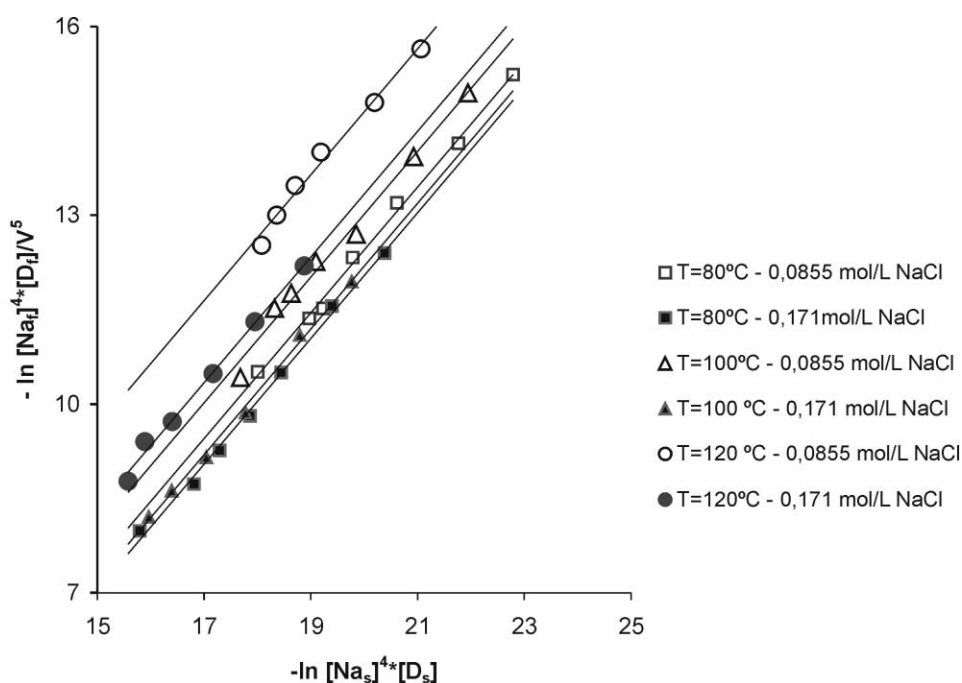

Fig. 7. Lineal regression curve of dyeing equilibrium experimental results with Freundlich isotherm.

Table 1
Calculated results of linear regression curve of experimental results with Freundlich isotherm ("x" = 1)

| Experimental | | Group | Correlation | Internal volume | Affinity |
| | | k | r^2 | V (l/kg) | $-\Delta\mu°$ (J/mol) |
T (°C)	NaCl (mol/l)				
80	0.0855	−7.55	0.9962	0.55	22,125
80	0.1710	−7.96	0.9957	0.47	23,329
100	0.0855	−6.98	0.9876	0.45	21,627
100	0.1710	−7.81	0.9969	0.34	24,173
120	0.0855	−5.36	0.9865	0.54	17,477
120	0.1710	−6.66	0.9937	0.33	21,744
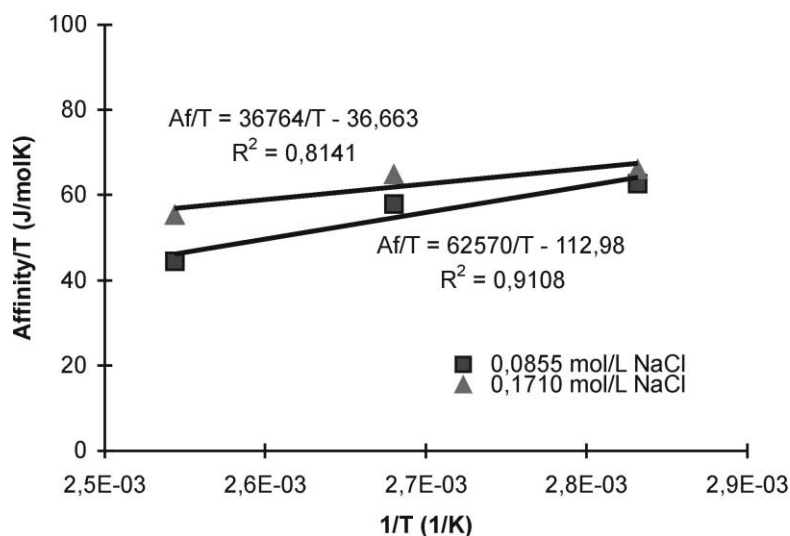
Fig. 8. Graphical representation of $-\Delta\mu°/T$ term (J/mol K) versus $1/T$ (1/K) to determined standard and entropy of dyeing.

increase of the temperature leads a reduction of this magnitude.

Eq. (7) could be used to calculate the dyeing standard entropy and enthalpy. The results of the linearization process and their graphical presentation are shown in Table 2 and Fig. 8.

As can be observed the data from the enthalpy calculation is −62,570 and −36,764 J/mol when

Table 2
Calculated results from lineal regression of Eq. (7)

NaCl (mol/l)	Linear regression	r^2	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol K)
0.0855	$-\Delta\mu°/T = 62{,}570/T - 113$	0.91	−62,570	−113
0.171	$-\Delta\mu°/T = 36{,}764/T - 37$	0.81	−36,764	−37

the electrolyte concentration is 0.0855 and 0.171 mol/l, respectively. With these values we can estimate the dyeing equilibrium constant, K, for given operational conditions.

4. Conclusions

The analysis and understanding of the adsorption isotherms of C.I. Direct Blue 1 on lyocell fibres, with the standard known isotherms—Nernst, Freundlich and Langmuir, shows that the Freundlich isotherm equation is best able to correlate adsorption data.

The model permits the design of a generalised calculation scheme that predicts the experimental results satisfactorily and provide information

about the equilibrium saturation uptake of dye by the fibre and also predict the dyebath exhaustion for a given dyebath concentration under the experimental conditions of temperature and electrolyte concentration used.

The free internal volume has been calculated for the lyocell fibre. We propose a value for V of 0.51 and 0.38 l/kg with a salt concentration of 0.0855 and 0.1710 mol/l, respectively.

Also, the characteristic thermodynamic magnitudes (standard enthalpy, entropy and affinity) that govern the dyeing process lyocell–C.I. Direct Blue 1 have been determined. These magnitudes allow estimating the equilibrium constant, K, for a given temperature and salt concentration.

Acknowledgements

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