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Evaluation of a dye isotherm method for characterisation of the wet-state structure and properties of lyocell fibre

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Abstract

An isotherm model based on classical thermodynamic principles has been explored as a route for characterisation of lyocell and comparative cellulosic fibres. The technique requires the experimental measurement of a dye isotherm, in this work Direct Blue 71, under conditions which avoid dye-site saturation and which maintain the influence of Donnan equilibrium upon the extent of uptake. The use of two salt levels was necessary for effective model fitting, which could be performed to establish values for both the fibre internal accessible volume and the free energy associated with dye–cellulose adsorption. The data could also be manipulated to determine the apparent anionic functionality of the fibre, in good agreement with published analytical results. The model has provided insights into the influence of fibre structure on dyeing and has also been valuable as a tool for interpreting the effect of fibre's physical and chemical processing on accessibility.

Keywords: Lyocell; Direct dye; Isotherm; Free energy; Accessibility; Structure; Properties; Nernst; Carboxyl; Anionic; Charge; Donnan equilibrium; Sodium hydroxide; Caustic treatment; Viscose

1. Introduction

The pioneering work on the physical chemistry of cellulosic fibre dyeing was conducted during the first part of the 20th century, over the life of the development and commercialisation of the class of direct dyes. Most of the theoretical thinking originates from this time, based on the classical concepts in thermodynamics, which were set out in the late 19th century. References to the models and theoretical treatments are found to be in all the main dyeing textbooks, which have clearly stood the test of time and therefore probably still represent the best foundation of knowledge within the dyeing industry [1–3]. Most importantly, it was recognised that study of the uptake of direct dyes could be used in the comparison of the internal structure of man-made cellulosic fibres, produced via different manufacturing routes or following different chemical treatments.

Lyocell is a relatively new cellulosic fibre, manufactured using a novel direct dissolution route. The commercial process utilises *N*-methylmorpholine-*N*-oxide monohydrate as the solvent, which dissolves cellulose at elevated temperature [4]. The viscous solution is extruded and drawn through a cooling air-gap before being coagulated in a dilute aqueous spin-bath. Phase separation lead to the formation of a fibrillar texture, equivalent to that found in viscose type polynosic fibres, which has excellent longitudinal continuity but weak lateral continuity [5,6]. This structure differs from that of regular textile grade viscose fibre, which is formed by extrusion of a temporary cellulose xanthate solution directly in a regenerative acid spin-bath. The partially

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regenerated filaments are drawn in the gel-state, which leads to a more poorly oriented fringe-micelle morphology in the final fibre [7].

The high wet-state porosity of lyocell, and the highly interconnected laminar nature of the interfibrillar pore spaces are believed to be at least partly responsible for the excellent dyeing characteristics of the fibre [8–11]. This is despite its relatively high crystallinity and high dry and wet-state tensile properties, which might be expected to be indicative of lower dyeability towards that of cotton. In fact there is consistent agreement that under a range of conditions lyocell achieves a dye uptake and dyeing efficiency equivalent to viscose, which has a higher porosity, lower crystallinity, and much lower wet and dry tensile properties [11,12]. Moreover, the caustic treatment of lyocell is known to lead not only to an increase in crystallinity but also to an increase in porosity, which is accompanied by a significant enhancement in dye uptake [13–16]. A simple ranking of dyeing performance based on conventional measurements of fibre structure may therefore be confusing. The interpretation of differences appears to depend on a more complex interplay of fibre characteristics identified in the original physical chemistry models.

The theoretical modeling work carried out, developed by Peters and Vickerstaff, based on earlier work by Neale and Stringfellow, was partly conceived as a way or rationalizing the already known differences in dyeing behaviour of different cellulosic materials [17–19]. The model has a number of merits in terms of its mathematical simplicity and its description of understandable physical properties. This gives it advantages over later more refined versions requiring more input parameters, or other models relying on parameters with less intuitive physical meaning [20–24].

An initial investigation was planned in keeping with the experimental procedures of Peters and Vickerstaff [18,19]. This required the measurement of a series of dye isotherms, allowing uptake to equilibrate between fibre and dyebath, at a range of dye concentrations, with comparisons at different levels of added salt. The intention of the current study was to critically examine the chosen model, with reference to other variants, and to consider its application as a practical technique for fibre characterisation. The use of now routine spreadsheet and graphical programs enables more effective data manipulation, offering the potential for new interpretational insights. A renewed application of the model may therefore provide a fuller understanding of the structural and other factors affecting the dyeing and wet-state processing of lyocell and other man-made cellulosic fibres. A practical methodology would also be invaluable in providing an explanation for the changes in lyocell properties caused by alterations in processing conditions or by chemical treatments, which will form the basis of future investigations.

2. Theory

The Peters and Vickerstaff model assumes that the chemical potential (μ) for a direct dye (D) can be expressed in terms of its activity (A) according to Eq. (1), where μ° is the chemical potential of the standard state, R is the gas constant and T the absolute temperature. The approximation is also made using electrolyte-solution theory that the activity of the dye corresponds to the product of the concentrations of its constituent ions, according to Eq. (2), where z is the ionic charge of the dye. The dye anion and its counter ions (usually Na^+) are assumed to move together in close association, in order to preserve electrical neutrality, so that the chemical potential will take an account of the environment of both species, within the dyebath and also within the internal fibre pore spaces.

$$\mu = \mu^{\circ} + \mathrm{R}T\ln(A) \tag{1}$$

$$A = \left[\mathrm{D}^-\right]\left[\mathrm{Na}^+\right]^z \tag{2}$$

The anion of the direct dye is substantive towards cellulose and will tend to move from the external dye solution into the fibre. An equilibrium is reached when the chemical potential (μ) of the dye is the same on each side of the fibre boundary, which leads to an expression for the standard change in chemical potential ($-\Delta\mu^{\circ}$). This is alternatively described as the standard affinity of the dye, or the standard free energy of dyeing ($-\Delta G^{\circ}$), according to Eq. (3), where (A_s) and (A_f) represent the dye activities in the dyebath solution and fibre, respectively.

$$-\Delta G^{\circ} = -\Delta\mu^{\circ} = \mathrm{R}T\ln\left(A_f/A_s\right) \tag{3}$$

The important feature of the activity terms is that they involve the freely moving cations as well as the substantive anions, so the position of the dye equilibrium will depend on the concentration of added salt. Eq. (3) is equivalent to a Nernst type isotherm and can be used to predict the partitioning of dye between the fibre and dyebath, provided the salt concentrations inside and outside the fibre and the standard free energy of dyeing are known. Alternatively, as with this work, it is possible to use Eq. (3) to determine the free energy of dyeing from the experimental isotherm curve. However, several complications exist, which have been addressed by Peters and Vickerstaff [18,19] and later by other workers [19–21,24–26].

Firstly, although the amount of dye on fibre [$\mathrm{D_f}$] at equilibrium can be determined from either the depletion of the dyebath or by extraction from the fibre, the units will be expressed in moles per kilogram of cellulose and not in moles per litre as required for Eqs. (2) and (3). A factor V is introduced which describes the internal volume of the fibre and modifies the activity term for the fibre phase to give Eq. (4) (where the charge signs have been dropped for clarity). The concentrations of both the adsorbed and internal free dye are included within this volume as they are considered to exert an identical influence on the chemical potential. The factor V with units of litres per kilogram converts concentrations to a volume basis, but also has some physical meaning in that it represents the internal pore or void space of fibre that is accessible to the dye. Peters and Vickerstaff and others appreciated that this parameter could be used to contrast different fibre structures, which will form a central element of the discussions in this current paper [1,18,19].

$$A_{\mathrm{f}}=\frac{[\mathrm{D_f}]\,[\mathrm{Na_f}]^{z}}{V^{z+1}}\ (\mathrm{mol/l}) \tag{4}$$

Secondly, the concentration of sodium ions within the fibre, $[\mathrm{Na_f}]$ in Eq. (4), is not measurable directly and must be deduced using Donnan membrane equilibrium theory, which relates the concentrations of all diffusible ions across the fibre boundary [1,2]. Peters and Vickerstaff derived Eq. (5) for calculation of $[\mathrm{Na_f}]$, expressed in terms of measurable or deducible quantities except for the accessible volume (V).

$$[\mathrm{Na_f}]=0.5\left\{z[\mathrm{D_f}]+\left(z^2[\mathrm{D_f}]^2+4V^2[\mathrm{Na_s}]\,[\mathrm{Cl_s}]\right)^{0.5}\right\}\ (\mathrm{mol/kg}) \tag{5}$$

To establish a value for the accessible volume (V) Peters and Vickerstaff were obliged to carry out a fitting exercise, based on the assumption of a linear unitary relationship between the logarithms of dye activities in the solution and the fibre, accordingly by reworking Eq. (3) to give Eq. (6). The model parameter V is adjusted to get a best linear least-squares fit, which should be independent of both dye and salt concentrations.

$$\log\left(A_{\mathrm{f}}\right)=\log(A_{\mathrm{s}})+\frac{\Delta G^{\mathrm{o}}}{2.303\mathrm{R}T} \tag{6}$$

Thirdly, the ionic concentrations in the solution phase required in Eq. (5) are a function of both the concentration of added salt and dye, and also the partitioning assumed from Donnan theory. An assumption was made that the large excess of the bath volume over the internal fibre volume would ensure that the equilibrium chloride concentration in the bath $[\mathrm{Cl_s}]$ would not deviate significantly from the value corresponding to the added salt. It was also assumed that the final concentration of sodium ions in the solution phase $[\mathrm{Na_s}]$ would be equivalent to the sum of all counter anions, according Eq. (7), which would include chloride and also the dye in solution measured by colorimetry.

$$[\mathrm{Na_s}]=[\mathrm{Cl_s}]+z[\mathrm{D_s}]\ (\mathrm{mol/l}) \tag{7}$$

The dye activity in the solution phase (A_{s}) required for Eq. (3) is then established according to Eq. (8).

$$A_{\mathrm{s}}=[\mathrm{D_s}][\mathrm{Na_s}]^{z}\ (\mathrm{mol/l}) \tag{8}$$

Finally, the presence of additional anionic sites within the fibre due to dissociated carboxylic functionality will influence the equilibrium of all the ions, and will therefore affect the internal dye activity. Such species would be present as a result of oxidation of cellulose chain ends or ring hydroxyl groups, occurring during pulp pretreatment of the manufacture and regeneration of the fibre spinning solution [27,28]. Deliberately oxidized cotton has been prepared which gave rise as expected to reduced dyeing behaviour [17]. Peters and Vickerstaff suggested that the additional carboxyl anion content would carry a stoichiometric quantity of sodium counter ions, which would add to the internal fibre sodium ion concentration $[\mathrm{Na_f}]$ predicted from the Donnan equilibrium. Eq. (5) can therefore be corrected to give Eq. (9), provided a suitable value for the carboxyl concentration on fibre $[C]$ can be determined. Carboxyl group analysis can be carried out by a direct chemical or spectroscopic method.

$$[\mathrm{Na_f}]_{\mathrm{cor}}=0.5\left\{z[\mathrm{D_f}]+\left(z^2[\mathrm{D_f}]^2+4V^2[\mathrm{Na_s}][\mathrm{Cl_s}]\right)^{0.5}\right\}+[\mathrm{C}]\ (\mathrm{mol/kg}) \tag{9}$$

3. Experimental

Stocks of factory produced 1.3 dtex lyocell and 1.4 dtex viscose were made available in loose fibre form, courtesy of Lenzing A.G. These fibres were used for experimental work without further treatment.

A batch of the lyocell fibre was immersed in an excess of a 10% weight/volume solution of sodium hydroxide (analytical grade). After steeping for 10 min, to ensure full wetting and swelling, the loose fibre mass was then rinsed in repeated quantities of hot water until the washings were at neutral pH. Further rinses were carried out with distilled water to ensure removal of all residual salt, the fibre was then squeezed and spread to dry under ambient laboratory conditions. The residual sodium content of the causticised lyocell fibre was determined by IPC-OES analysis of a soxhlet water extract of the fibre. This procedure was carried out to confirm the efficiency of removal of alkali ions, which otherwise might influence dyeing behaviour.

Two sets of isotherm dyeings were carried out for each of the as-received lyocell and viscose fibre samples and the causticised lyocell sample. A commercial supply of Direct Blue 71 dye was used, at 95% purity containing 5% sodium carbonate. Solutions of the dye were made up at six concentrations, to give from 0.33 up to 2.0 wt% on fibre, using either 2 or 4 g/l stock solutions of sodium chloride. Samples of the initial dyebath solutions were collected for subsequent spectroscopic analysis. Portions of 100 ml of the made up solutions were transferred to 200 ml stainless-steel dyeing tubes which were pre-heated to 80 °C using a Mathis Labomat laboratory scale dyeing machine. After temperature equilibration, 5 g of fibre was added to each pot, at 20:1 liquor ratio, with dyeings being continued at 80 °C for 2 h. At the end of the time the final solutions from each dye-pot were sampled in turn, ensuring no reduction in temperature below the 80 °C set point. A preliminary investigation had been carried out to determine a practical time of dyeing under these specific conditions, in order to reach full dyeing equilibrium. The use of loose fibre provided excellent transfer between fibre and bath and meant that a relatively moderate time was feasible, in contrast with the much longer times reported for equilibration using woven fabrics [19,22].

Further samples from both lyocell and viscose stocks were soxhlet extracted in methanol, to remove the low level of PEG–fatty acid applied as spin-finish. These two stripped samples and two corresponding as-received samples were dyed under exhaust conditions, with 12.3 mmol/kg on weight of fibre of Direct Blue 71 dye, at 20:1 liquor ratio, with 2 g/l sodium chloride, at 80 °C for 2 h. This exercise was to determine if presence of factory spin-finish treatment had any influence on the equilibrium dye uptake as required for the isotherm analysis.

A further set of equilibrium dyeings was carried out with a constant dye to salt weight ratio of 1:10 by weight, to explore the progress towards saturation behaviour of Direct Blue 71 dye on both viscose and lyocell. Dyebath solutions were made up with concentrations increasing from 0.2 to up a maximum of 20% by weight on fibre, with dyeings carried out as before for 2 h at 80 °C at 20:1 liquor ratio.

All initial and final dye solutions were diluted by appropriate ratios, to adjust the absorbance to a measurable range. Dye concentrations were determined from a Beer's law plot at 589 nm, with units expressed in millimoles per litre or per kilogram of dry fibre for the modeling studies, after making small corrections for purity (dye mol. wt = 1299, $z = 4$). The small amount of salt added with the dye was expressed as the sodium chloride molar equivalent. Accurate as-received fibre weights were converted to a moisture-free basis using separately determined regain values. Microsoft Excel software was used for all data manipulation and modeling.

The total pore capacity of the fibre samples was determined separately by the centrifugation method for water retention. Approximately 1 g duplicate portions of fibre were immersed in distilled water for 10 min. Centrifugation was carried out using capped tubes at 3000 rpm for 15 min, using a machine with a 10-cm radius carousel (centripetal force = 1300G). Centrifuged samples were accurately weighed and then dried for 18 h at 60 °C before reweighing. Water retention (WR) was calculated according to Eq. (10)

$$\mathrm{WR} = 100 \times \frac{(\text{centrifuged weight} - \text{dried weight})}{\text{dried weight}} \tag{10}$$

4. Results and discussion

Dye isotherms for all three fibre samples at both salt concentrations are shown in Figs. 1 and 2. Data from the single dyeings of spin-finished and stripped fibres are shown in Table 1.

The method of Peters and Vickerstaff requires the plotting of $\log(A_f)$ against $\log(A_s)$, adjusting the fibre internal volume parameter (V) until a best-fit straight line is achieved, theoretically with unit gradient. The fitting errors during this process were found to be relatively insensitive to V unless data at both salt concentrations were combined. The overall goodness of r^2 achieved in the fitting exercise is excellent, as shown in Fig. 3, especially considering that the data are from two separate isotherm experiments. The values of r^2 show a broad but defined maximum with adjustment of V, illustrated in Fig. 4, which suggests that the method can be utilised to establish a characteristic accessible volume for each fibre sample. With care it was possible to fix V with ± 0.1 ml/g cellulose, the use of two salt levels being the key to the usefulness of the technique, as originally explored by Peters and Vickerstaff. The fitted

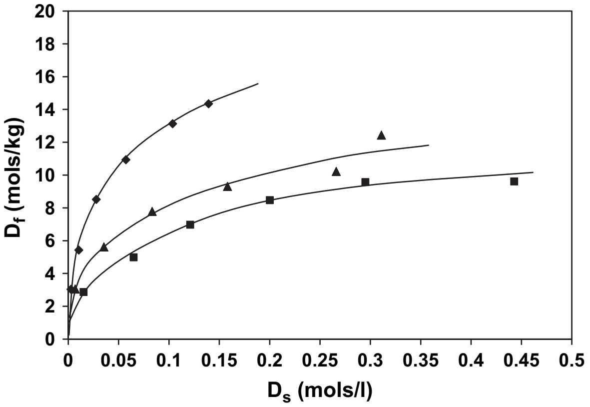

Fig. 1. Direct Blue 71 adsorption isotherm at 2 g/l NaCl at 80 °C. Causticised lyocell (◆), lyocell (▲), viscose (■).

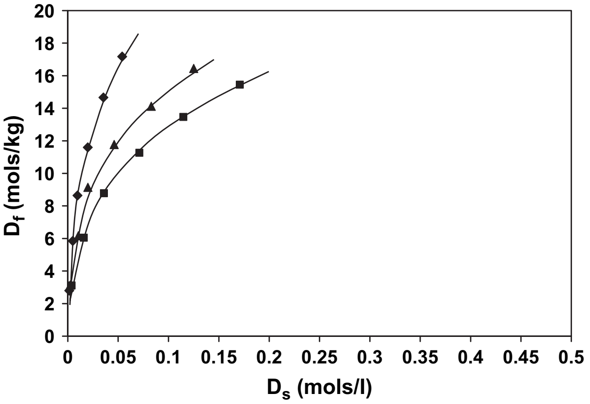

Fig. 2. Direct Blue 71 adsorption isotherm at 4 g/l NaCl at 80 °C. Causticised lyocell (◆), lyocell (▲), viscose (■).

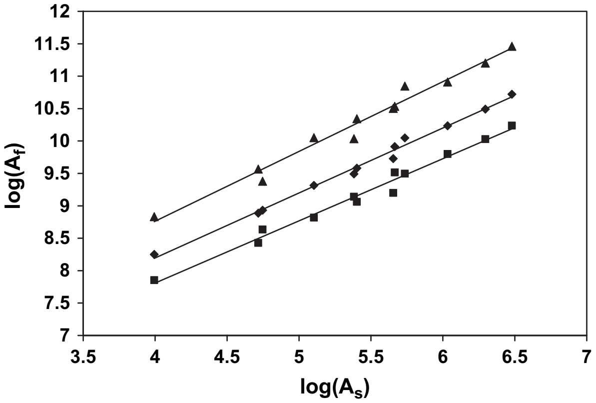

Fig. 3. Linear fit for Peters and Vickerstaff model with varying accessible volume (V); 0.3 ml/g (▲), 0.45 ml/g (◆), 0.6 ml/g (■).

results for all the three fibres are summarised in Table 2, together with total water pore capacities from the water retention method.

Peters and Vickerstaff noted that a downward trend in ΔG^o calculated from Eq. (3) with increasing applied dye could be interpreted as evidence of the presence of carboxyl groups on the fibre, disturbing the ionic equilibrium and increasing the internal sodium concentration [Na_f]. Their simple modification assumes that each carboxyl group carries a sodium counter ion, leading to Eq. (9). Following this modification, the free energies of dyeing at both salt levels are then plotted against log(A_s), the data for as-received lyocell are shown in Fig. 5. Careful adjustment of the model value for carboxyl content (C) was carried out to correct the variation in free energy across the dye concentration range, without recourse to separate analysis. This approach was found to be quite sensitive to small adjustments, so a horizontal fitted line could be established to within a few milli-equivalent units. The best fitted values for carboxyl content are compared in Table 2 with those reported in the literature for lyocell and viscose (C_{ex}), established by titration against alkali [28]. The final constant values of ΔG^o for each fibre sample are also shown in Table 2.

Table 1
Influence of spin-finish on equilibrium exhaust dyeing of fibres with Direct Blue 71 (20:1 liquor ratio, 2 g/l sodium chloride)

Sample	Initial bath concentration (mmol/l)	Final bath concentration (mmol/l)	Dye concentration on fibre (mmol/kg-cellulose)
Lyocell: as-received	0.62	0.12	10.63
Lyocell: stripped	0.62	0.14	10.35
Viscose: as-received	0.62	0.20	9.05
Viscose: stripped	0.62	0.20	9.07

Fitting attempts for the three samples reveal differences in the free energy of dyeing, although the group of results is similar in magnitude to those determined from earlier published data on direct dyes [21,22]. The values for Direct Blue 71 on standard viscose and lyocell are similar, around 28 kJ/mol, which is in agreement with the view that dye adsorption occurs by the same mechanism regardless of the morphological history of the cellulose surface.

Previous workers have been convinced by the physical significance of the accessible internal volume term (V), which is established by fitting to Peters and Vickerstaff's and other thermodynamic models [1]. A general correlation between water retention (WR) has been found, this measurement representing the total hydrated fibre pore volume. The value would be expected to be higher than the volume determined by dye adsorption, the larger molecular size restricting its accessibility within the fibre structure. The water retention of viscose is higher than lyocell, at 0.90 compared to 0.68 ml/g, although dyeing studies at low salt concentrations have shown that lyocell gives rise to higher dye adsorption than viscose [12]. This work

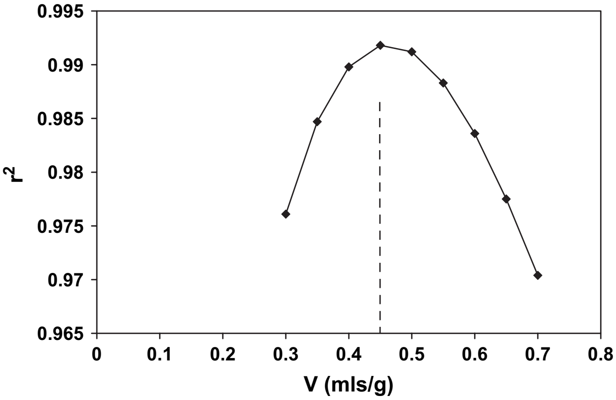

Fig. 4. Variation in r^2 correlation of log(A_f) vs. log(A_s) with adjustment of accessible volume (V) for lyocell adsorption isotherm data.

Table 2
Direct Blue 71 dye isotherm fitted parameters and comparative values for lyocell and viscose fibres

Sample	WR − water retention (l/kg)	V − model fit (l/kg)	C − model fit (mequiv/kg)	C − model fit (mequiv/kg) predicted in total pore volume	C_{ex} − titration (mequiv/kg)	ΔG^o − free energy of dyeing (kJ/mol)
As-received lyocell	0.68	0.45 ($r^2 = 0.991$)	9	14	19[a]	27.5
As-received viscose	0.90	0.39 ($r^2 = 0.991$)	16	37	41[a]	28.5
Causticised lyocell	0.83	0.86 ($r^2 = 0.998$)	3	3		23.5
Causticised lyocell + 0.5 g/l salt correction	0.83	0.69 ($r^2 = 0.999$)	7	–	–	25.0
Causticised lyocell forced $\Delta G^o = 28$ kJ/mol	0.83	0.56 ($r^2 = 0.951$)	9	–	–	28.0[b]

[a] Data from Ref. [28].
[b] Forced fit.

suggests that the actual accessible volume for dye uptake may be higher for lyocell, which is consistent with the results of the isotherm fitting presented in Table 2, showing lyocell with an accessible volume of 0.45 compared to 0.39 ml/g for viscose. The presence of a higher proportion of accessible pore spaces in lyocell is also indicated from studies using the inverse size exclusion technique [29–31].

The current study confirms that the enhanced dye uptake of caustic treated lyocell can be explained on the basis of an increase in accessible internal volume, which is in keeping with known effects of mercerisation on cotton [32,33]. The model value for accessible volume is raised significantly to 0.86 ml/g, which is actually slightly higher than the total volume determined from water retention. This is a partial failure in the model, although it is interesting to note that a similar exaggerated increase in the accessible volume was determined from earlier studies on cotton by Marshall and Peters [19]. Here the effect of mercerisation increased the model fitted V term from 0.3 to 0.5 ml/g, a change of 66%, compared to a change of only 22% in water retention. The current data for causticisation of lyocell show an 80% increase in V in contrast with a 22% increase in water retention.

One possible explanation for the exaggerated value of accessible volume following lyocell causticisation is the contamination of the dyebath by residual sodium ions from the alkali. A manipulation of the spreadsheet suggests that a lower fitted V value of 0.69 ml/g would be returned if the actual dyebath salt concentrations were raised by 0.5 g/l, as illustrated in Table 2. However, this represents an unrealistic level of contamination, and in fact no sodium ions were detected in the solution from the soxhlet extracted sample. A further possibility was that the removal of the spin-finish by alkali treatment would promote more efficient dye uptake. However, the results from the separate study summarised in Table 1 show that this is not the case. Removal of finish by organic extraction led to no significant change in equilibrium dyeing, with the differences between viscose and lyocell remaining constant.

Causticisation of lyocell is a drastic treatment, which leads to strong lateral fibre swelling and subsequent relaxation of orientation, coupled with an increase in crystallinity [13–15,33,34]. Presumably the pore texture has been manipulated as well as the total pore volume, which may have a positive effect on the proportion of surface sites available for dye adsorption. The pore shape factor may move more fully towards a lamellar rather than a cylindrical form, which would not be accounted for by the accessible volume term of the model. The lower fitted free energy of dyeing of 24 kJ/mol may also be construed as evidence of a change in internal surface character, although this counters the expectation that higher dye uptake will correspond to higher standard free energy. A forced fit with a free-energy of 28 kJ/mol leads to a volume term of 0.56 as

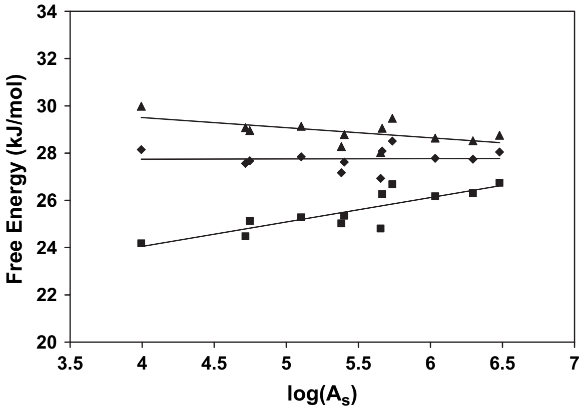

Fig. 5. Variation in constancy of free energy of dyeing of lyocell from Peters and Vickerstaff model with adjustment of fibre carboxyl group content (C); 0 mequiv/kg (▲), 9 mequiv/kg (◆), 16 mequiv/kg (■).

shown in Table 2, which is a more moderate increase over the original value for lyocell, but is reached with a much r^2 correlation.

Alternatively, it has been proposed that variations in the free energy of dyeing may be diagnostic of changes in internal surface chemistry [35]. The cellulose polymer chains at the solution-facing pore surfaces are oriented to expose a layer of hydroxyl groups, which take part in hydrogen bonding with adjacent molecules. The entire surface therefore becomes more hydrophilic and might therefore be expected to interact more effectively with the dye. However, if hydrophobic type interactions are responsible for dye substantivity then it could be argued that these will be reduced by an improvement in internal surface crystallinity. Other theories for substantivity propose a loss of the water of solvation of the dye due to interaction with internal cellulose hydroxyl groups, leading to aggregation or precipitation of the dye within the fibre [1,21]. This effect would possibly be less efficient at higher pore volume. The exact mechanism of adsorption of direct and reactive dyes is still a subject for debate [36,37].

The model can be used to predict the effect of accessible volume V on dye partition ratio (D_f/D_s) at different added salts concentrations, shown in Fig. 6a. A positive linear relationship exists at constant ΔG^o and $[D_s]$, with the increase in salt concentration resulting in a raise of D_f through a reduction in the ratio of N_f/N_s. This results in an increased sensitivity to the partition ratio to changes in the V term. In a practical situation, however, the depletion of the dyebath will make the determination of D_s prone to error, so the arrangement of partial bath exhaustion is therefore advisable, achieved at higher salt levels by decreasing the amount of fibre (increasing the liquor ratio).

The fitting approach adopted for the current work allows the V term for each fibre sample to be fixed independently of any subsequent fitting to establish a value for fibre carboxyl functionality. The model carboxyl contents established for each fibre sample are summarised in Table 2, the higher value for viscose compared to lyocell being consistent with published analytical data [28]. The magnitudes of the model fitted values are lower than determined by alkali titration, which may be due to the reduced accessibility to carboxyl functionality achieved by the large Direct Blue 71 dye molecule, compared to the much smaller hydroxide ion. Table 2 also shows a further correction to the model fitted carboxyl contents, scaled by the ratio of total volume to accessible volume. These apparent total carboxyl contents are gratifyingly close to those determined by titrimetric analysis.

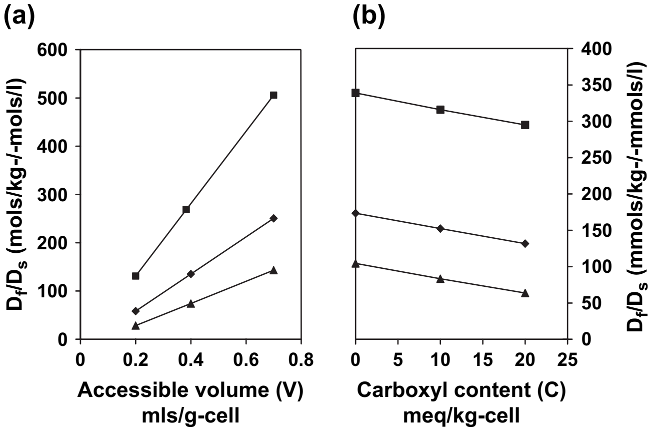

Fig. 6. Peters and Vickerstaff model prediction of the effect of accessible volume (V) and fibre carboxyl content (C) on partition ratio of Direct Blue 71. With $D_s = 0.1$ mmol/l and $\Delta G^o = 28$ kJ/mol; 2 g/l NaCl (▲), 4 g/l NaCl (◆), 10 g/l NaCl (■).

The model also suggests a lowering of carboxyl content after causticisation of lyocell, a phenomenon that has been described by workers evaluating the uptake of cationic dyes by cellulosic fibres [38]. Most likely the alkali swelling action has allowed the removal of low molecular weight cellulose fragments, which will carry a proportionally higher content of carboxyl end-groups.

The Peters and Vickerstaff model allows a prediction of the influence of fibre carboxyl content on dye uptake characteristics, as illustrated in Fig. 6b. A negative linear relation with D_f/D_s is seen at fixed ΔG^o and D_s, with a constant slope but with variable offset, as expected from influence on Na_f from Eq. (9). Thus the relative influence of carboxyl functionality is expected to be more exaggerated when dyeing at low salt contents and may be masked at the higher salt concentrations usually recommended for direct and reactive dyes.

Other workers have explored variations of the Peters and Vickerstaff model in an attempt to establish a more detailed physical description of fibre–dye surface interactions. A modified Langmuir model was developed by Daruwalla and D'Silva, which assumes that the dye is adsorbed at discrete sites on the internal cellulose surfaces, whilst the sodium ions diffuse freely [20]. The modified Eq. (11) was developed for the activity of the dye in the fibre, where symbols have the meanings as before but a saturation term (D_t) accounts for limiting the occupation of all available sites [23]. This model was found to lead to a successful linear fit to a $\log(A_f)/\log(A_s)$ plot, as illustrated for lyocell in Fig. 7.

$$A_f = \frac{[D_f]\,[Na_f]^z}{([D_t] - [D_f])\,V^z}\ (\text{mol/l}) \tag{11}$$

However, both V and D_t require adjustment in the fitting exercise, and as expected from Eq. (9) it was found that the correlation (r^2) improved continuously with increasing values of D_t. In addition, the current isotherm measurements up to 2% dye on fibre represent a region which is probably still far from saturation,

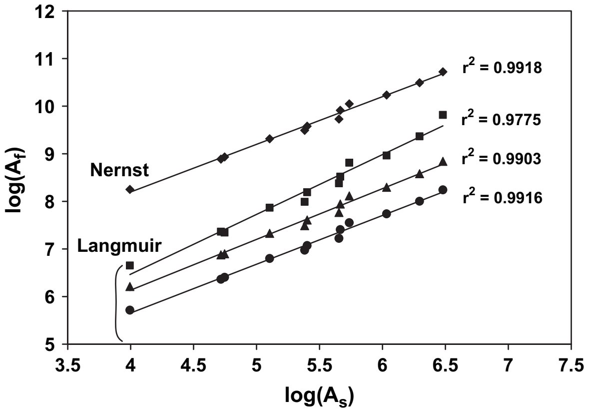

Fig. 7. Correlation of log(A_f) and log(A_s) from Langmuir type model of Darawalla et al. Direct Blue 71 adsorption isotherm data for lyocell, with accessible volume (V) at 0.45 ml/g and (C) at 9 mequiv/kg-cell. Dye saturation (D_t) adjusted, 20 mmol/kg (■), 50 mmol/kg (◆), 150 mmol/kg (◆). Comparison with Nernst type model of Peters and Vickerstaff (●).

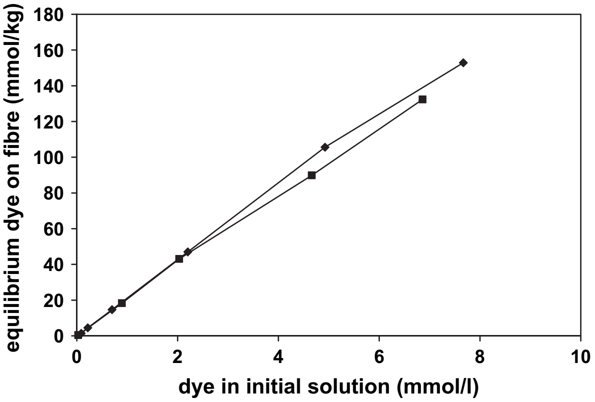

Fig. 8. Equilibrium build-up curve for Direct Blue 71 on lyocell (■) and viscose (◆), at 80 °C with constant ratio 10:1 (wt/wt) of added NaCl to dye.

where the influence of competition for surface sites will not be valid. Independent measurements of dye saturation have been attempted to satisfy the requirements of the model but this adds to the complexity of the methodology [20,21]. Vickerstaff has questioned whether discrete adsorption is an appropriate mechanism, doubting that the surface electric double layer which some workers have described will be able to exist within the confines of the fibre pores [1]. Peters and Vickerstaff favour a less structured diffuse adsorption of the dye, which is in keeping with the hypothesis that the loss of the hydration shell of the dye molecule is responsible for its affinity for cellulose. There is no need to consider saturation at a single monolayer of adsorbed dye and its activity in the fibre is limited purely by the development of the Donnan membrane potential.

From a theoretical standpoint the accessible volume term is independent of salt concentration, which means that the data from a conventional build-up experiment may be suitable for analysis using the Peters and Vickerstaff technique. This makes it possible to directly explore the relevance of saturation with respect to the model, by extending dye uptake to very high levels on fibre. The build-up curves acquired for lyocell and viscose are shown in Fig. 8, with solutions made up at a constant salt to dye molar ratio of 188 to 1 (10:1 by weight). The curves are linear at low dye levels but deviations at higher concentration may suggest a change in behaviour of dye within the pore structure, which is more pronounced for lyocell than viscose. The previously acquired values for accessible volume and carboxyl content for each fibre were used to calculate the free-energy of dyeing at all concentrations, as shown in Fig. 9. The values for both fibres appear constant at low concentrations, although lower for lyocell compared to viscose. This difference is more apparent than determined from the first isotherm experiments, in Table 2. Both fibres reveal a reduction in free energy approaching high dye uptakes [D_f] at around 80 mmol/kg for viscose and 50 mmol/kg for lyocell, and it is tempting to ascribe this to the onset of saturation of the internal fibre surfaces. The inflection points are broadly in agreement with quoted saturation values for man-made cellulosics [1], however, in no sense does the dye uptake reach a limiting plateau and it is more reasonable to assume a change from monolayer coverage to multiplayer aggregation. Although the data in Fig. 9 are not precise, the higher concentration inflection point for viscose fibre may suggest that the available surface area for monolayer adsorption is higher than for lyocell, despite its lower overall accessible volume (V). Possibly the size distribution of accessible pore spaces tends to lower average for viscose, with a correspondingly enhanced surface area. This is in keeping with the knowledge that the skin morphology of viscose gives rise to a reduced dye diffusion coefficient, due to its very fine pore texture [7]. This higher population of small pores may help to explain the higher free energy of dyeing

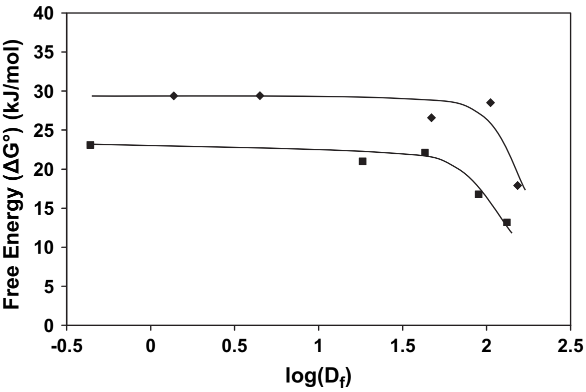

Fig. 9. Dependence of free energy of dyeing (ΔG^o) from Peters and Vickerstaff model using data from lyocell (■) and viscose (◆) build-up curves.

calculated for viscose from the Peters and Vickerstaff model.

5. Conclusions

The study has shown that the use of the Peters and Vickerstaff technique has considerable value as a tool for the interpretation and comparison of the wet-state properties of man-made cellulosic fibres. The model makes use of understandable physical parameters, of accessible volume (V) carboxyl functionality (C) and free energy of dyeing (ΔG^{o}) which can be fitted with good accuracy using isotherm data collected at two salt concentrations. Isotherm measurements are best carried out at low added salt contents, to maintain sensitivity to fibre carboxyl functionality and also to avoid dyebath depletion. The operation at high liquor ratios may also be advisable to achieve best accuracy. Isotherm measurements require completion of dye uptake to full equilibrium, which may take extended times for woven fabrics or for cast films, however, the use of free fibres permits experiments to be conducted over more manageable timescales. Alternative isotherm models make use of a fibre saturation value, which is not considered to be meaningful at low dye uptakes. The exploration of differences in fibre internal surface area will require the use of separate experimental methodologies, as isotherm measurements in themselves are not sufficiently sensitive to the trend from monolayer to multiplayer adsorption or to the phenomenon of aggregation.

The data collected using Direct Blue 71 dye are consistent with that reported for similar dyes in the literature. The accessible volume can be regarded as the pore volume within the fibre that is available to the test dye molecule. The model value is higher for lyocell than viscose, despite its lower total water retention, which suggests that lyocell has a higher proportion of larger pores. Causticisation raises the accessible volume of lyocell, which can be interpreted on the basis of the modification of the fibrillar structure of the fibre, and a further increase in the average pore size. The free energy of dyeing determined from the model can be thought of as describing the effectiveness of the internal pore spaces in promoting dye adsorption. Values for the fibres studied are broadly similar, suggesting the same general physical bonding mechanisms. The apparent reduction in free energy on moving to higher accessible volume is possibly related to an increase in average pore size. The fitting of a carboxyl correction term results in modeled values for carboxyl molar functionality that are in agreement with published analytical data, especially if the accessible volume of the test dye is taken into consideration. In summary, the Peters and Vickerstaff methodology will be extremely helpful in providing a structural basis for differences in dyeing or chemical uptake behaviour, caused by alterations in fibre production conditions or due to other chemical or physical processing.

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