Dyes and Pigments, Vol. 39, No. 4, pp. 243–258, 1998

Printed in Great Britain
PII: S0143-7208(98)00014-X 0143-7208/98/$—see front matter

Dissociation of Hydroxyl Groups of Cellulose at Low Ionic Strengths

Hiromi Motomura, Sook-Hee Bae & Zenzo Morita*

Department of Material Systems Engineering, School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

(Received 9 January 1998; accepted 3 February 1998)

ABSTRACT

According to Donnan equilibrium theory, the dissociation of the hydroxyl groups of cellulose (mercerized cotton) or alkaline adsorption can be treated as a function of the pH and ionic strengths of the external solution, and of the amount of fixed anionic groups in cellulose, by using 1:1- and 1:2-electrolytes as a neutral salt to adjust the ionic strength. The acid dissociation constant of the hydroxyl group for cellulose was estimated by Neale at 25°C, and this treatment therefore only holds for this temperature. The ratios of hydroxide ion concentrations in the inner solution and those in the external one, $[OH^-]_i/[OH^-]_s$*, as well as* $[Cell\text{-}O^-]_i/[OH^-]_i$*[*$Cell\text{-}O^-]_i$*: cellulosate ion concentration in the inner solution) decrease with a increase in the concentration of hydroxide ions in the external solution and the fixed anions in cellulose, and with a decrease in the ionic strengths in the external solution, but with little decrease of* $[Cell\text{-}O^-]_i/[OH^-]_i$*. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: reactive dyeing, dissociation of hydroxyl groups of cellulose, inner pH, coion exclusion, ionic strength.

INTRODUCTION

Alkaline adsorption by cellulose in the presence of sodium chloride as neutral salt was investigated by Sumner [1] on the basis of the Donnan adsorption

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*Corresponding author.

model. Since reactive groups of reactive dyes react with cellulosate ions, the dissociation of the hydroxyl groups of cellulose is indispensable for the reaction. The acid dissociation constant of the hydroxyl groups was determined by Neale [2] in 1930 only at 25°C.

McGregor *et al.* [3–5], on the other hand, has analyzed the role of ionizable carboxyl groups in the adsorption of anionic dyes on cellulose as a function of ionic strengths.

Sumner and Vickerstaff [6] reported the ratios of the concentrations of cellulosate and hydroxide ions in the external solution under various conditions at 25°C. These ratios have been used in discussions on the reactivity of cellulose with reactive dyes [7, 8]. Marshall [9–11] analyzed the relationships between the ratios at various ionic strengths and the external pH, on the basis of Sumner's results [1], but his treatment is inclined to the importance of high ionic strengths in the fixation of reactive dyes, and seems to contain some errors.

In the present paper, problems which occur when reactive dyeing is carried out under the conditions of low salt is examined according to the Donnan equilibrium model. The deviation of the hydroxide ion concentration in the inner surface of cellulose from that in the dyebath is analyzed over a wide range of ionic strengths and concentrations of fixed ionic groups in cellulose. In the simulation of present study, the dissociation of the hydroxyl groups for mercerized cotton is essentially examined as cellulose.

THEORETICAL

Symbols used

Suffixes, *f*, *s*, and *i*, denote the phases of cellulose (*fiber*), the external *solution*, and the *inner* surface of cellulose, respectively.

A	Ratio of $[\text{OH}^-]_i/[\text{OH}^-]_s$
B	Ratio of $[\text{Cell-O}^-]_i/[\text{OH}^-]_i$
C	Ratio of $[\text{Cell-O}^-]_i/[\text{OH}^-]_s$
$[\text{Cell–COO}^-]_f$	Concentration of carboxylato ions in cellulose (they are regarded to ionize completely at $\text{pH} > 7$)
$[\text{Cell–D}_1{}^{N-}]_f$	Concentration of fixed dye anion having N anionic groups in cellulose (mol kg^{-1})
$[\text{Cell–O}^-]_f$	Concentration of cellulosate ions in cellulose (mol kg^{-1})
$[\text{Cell–O}^-]_i$	Concentration of cellulosate ions in the inner solution of cellulose (mol dm^{-3})
$[\text{Cl}^-]_n$	Concentration of chloride ions in the nth phase (mol dm^{-3})

G	Concentration of glucoside unit [1000/(molecular weight of glucoside residue) = [1000 g kg^{-1}/162.14 g mol^{-1} = 6.17 mol kg^{-1}]×availability (= 1-crystallinity) (mol kg^{-1}) (cf. Table 1)
$[H^+]_n$	Concentration of hydrogen ions in the *n*th phase (mol dm^{-3})
I	Ionic strength (all the ionic species in the external solution are taken into consideration) (mol dm^{-3})
K_a^C	Dissociation constant of hydroxyl groups of cellulose (1.84×10^{-14} at 25°C) [2]
K_W	Ionic product of water (1.002×10^{-14} at 25°C [16]).
$[Na^+]_n$	Concentration of sodium ions in the *n*th phase (mol dm^{-3})
$[NaCl]_s$	Concentration of sodium chloride added to the external solution (mol dm^{-3})
$[NaOH]_s$	Concentration of sodium hydroxide added to the external solution (mol dm^{-3})
$[Na_2SO_4]_s$	Concentration of sodium sulfate added to the external solution (mol dm^{-3})
$[OH^-]_n$	Concentration of hydroxide ions in the *n*th phase (mol dm^{-3})
R	Gas constant
S	Sum of the concentrations of ionic groups fixed with cellulose = $[\text{Cell–COO}^-]_f + N[\text{Cell–D}_1{}^{N-}]_f$ (except for $[\text{Cell-O}^-]_f$) (eq. kg^{-1})
$[SO_4^{2-}]_n$	Concentration of sulfate in the *n*th phase (mol dm^{-3})
T	Absolute temperature (K)
V	Internal volume of cellulose ($\text{dm}^3\,\text{kg}^{-1}$) (cf. Table 1)

Dissociation of hydroxyl groups of cellulose

It is assumed in this paper that the activity coefficients of all the ionic species are unity. From the acid dissociation equilibrium for the hydroxyl groups of

TABLE 1
Values of Parameters Used for Calculating the Properties of Hydroxyl Groups in Various Cellulosic Fibres (range of observed values in parentheses)

	Cotton	*Mercerized cotton*	*Regenerated cellulose [1]*
Crystallinity (%) [13, 14]	80 (80~90)	60 (50~70)	26
Volume term ($\text{dm}^3\,\text{kg}^{-1}$), V [15]	0.22	0.26	0.45
Conc. of glucoside unit (mol kg^{-1}), G	1.23	2.47	4.57
Conc. of glucoside unit (mol dm^{-3}), G/V	5.61	9.49	10.15
Carboxyl groups content (mol kg^{-1}) [12]	0.005 (0.002~0.005)	0.010 (0.010~0.020)	0.040 (0.010~0.050)
Limiting value of $C(-)$	10.3	17.4	18.6

cellulose in the inner solution of cellulose, cellulosate ions can be represented by:

$$[\mathrm{Cell}-\mathrm{O}^{-}]_f = \frac{G\cdot K_a^C}{[H^{+}]_i + K_a^C} \tag{1}$$

where one of hydroxyl groups in each glucose unit is assumed to be able to dissociate. Since the values of K_a^C was determined only at 25°C [2], the present analyses hold for that temperature. If the ionic product of water is defined in the inner solution phase, in the same way as in bulk water, then $[\mathrm{Cell{-}O}^{-}]_f$ can be derived from eqn (1) as a function of $[\mathrm{OH}^{-}]_i$ as shown in eqn (2).

$$[\mathrm{Cell}-\mathrm{O}^{-}]_f = \frac{G[\mathrm{OH}^{-}]_i}{(K_W/K_a^C) + [\mathrm{OH}^{-}]_i} \tag{2}$$

Calculation of $[\mathrm{Na}^{+}]_i$ in presence of sodium sulfate

When sodium hydroxide is used as the alkaline agent to adjust the pH, and sodium sulfate is used as the neutral salt to adjust the ionic strength (when added to the dyebath), the activities of sodium sulfate and sodium hydroxide in both the phases may be assumed to be equal to each other, according to the Donnan membrane equilibrium theory [15–18]:

$$[\mathrm{Na}^{+}]_s^2[\mathrm{SO}_4^{2-}]_s = [\mathrm{Na}^{+}]_i^2[SO_4^{2}]_i \tag{3}$$

$$[\mathrm{Na}^{+}]_s[\mathrm{OH}^{-}]_s = [\mathrm{Na}^{-}]_i[\mathrm{OH}^{-}]_i \tag{4}$$

In water-swollen cellulose, the principle of electroneutrality holds as follows

$$V[\mathrm{Na}^{+}]_i + V[\mathrm{H}^{+}]_i - 2V[\mathrm{SO}_4^{2-}]_i - V[\mathrm{OH}^{-}]_i - [\mathrm{Cell}-\mathrm{O}^{-}]_f - S = 0 \tag{5}$$

where S is the sum of $[\mathrm{Cell{-}COO}^{-}]_f$ and $N[\mathrm{Cell{-}D}^{N-}]_f$ or the concentrations of the fixed ionic groups at pH > 7, except for the concentrations of cellulosate ions depending upon the pH.

Here, when parameter y, (the ratio of the concentrations of sodium ions in both the phases) is defined by:

$$y = [\mathrm{Na}^{+}]_i/[\mathrm{Na}^{+}]_s, \tag{6}$$

the concentrations of sulfate and hydroxide ions in cellulose phase may be represented by:

$$[\mathrm{SO}_4^{2-}]_i = [\mathrm{SO}_4^{2-}]_s/y^2 \tag{7}$$

$$[\mathrm{OH}^-]_i = [\mathrm{OH}^-]_s/y \tag{8}$$

The hydrogen ion concentration is similarly given by eqn (9), but may be negligible at pH $\geqq 7$, as

$$[\mathrm{H}^+]_i = K_w/[\mathrm{OH}^-]_i = K_w y/[\mathrm{OH}^-]_s. \tag{9}$$

On the other hand, the total concentrations of sodium, hydroxide, and sulfate ions in the external solution are, respectively, given by

$$[\mathrm{Na}^+]_s = 2[\mathrm{Na_2SO4}]_s + [\mathrm{NaOH}]_s \tag{10}$$

$$[\mathrm{OH}^-]_s = [\mathrm{NaOH}]_s \tag{11}$$

$$[\mathrm{SO}_4^{2-}]_s = [\mathrm{Na_2SO}]_s \tag{12}$$

If eqn (5) is described in terms of the external concentrations of all the species except for cellulosate ions by taking eqns (1) and (6–9) into consideration, eqn (5) can be rewritten as in eqn (13):

$$V[\mathrm{Na}^+]_s y - 2V[\mathrm{SO}_4^{2-}]_s/y^2 - V[\mathrm{OH}^-]_s/y - \mathrm{G}/\{1 + K_w y/(K_a^C[\mathrm{OH}^-_s])\} - S = 0 \tag{13}$$

A straight solution to obtain the roots of eqn (13) may be meant to solve a quartic equation with y or $[\mathrm{Na}^+]_i$ but may meet a difficulty in discriminating among four roots. Some considerations may thus be needed before this problem can be overcome. Thus, according to Sumner [1], $[\mathrm{OH}^-]_i \leqq [\mathrm{OH}^-]_s$, i.e. $y \geqq 1$; when $S=0$, y becomes unity at $[\mathrm{OH}^-]_s \ll 1$. If the left hand side of eqn (13) is equated to $f(y)$, $f(y)$ can be confirmed to be a monotonically increasing function at $y>0$, since $f'(y)>0$ at $y>0$.

Then, the function $f(y)$ has following relations:

$$f(1) < 0 \quad \text{at } y = 1 \tag{14}$$

$$f(\infty) \to \infty \ \text{at} \ y \to \infty \tag{15}$$

The function $f(y)$ is then continuous in this region of y and $f(y)$ must have at least a real root at $y \geqq 1$. Putting the initial value of y as unity, the root can be numerically obtained. When it is confirmed that the root fulfills eqn (5), by use of eqns (2) and (6)–(9), it is regarded to be the root.

Calculation of $[\mathrm{Na}^+]_i$ in presence of sodium chloride

When sodium chloride is used an neutral salt instead of sodium sulfate, the priniciples of electroneutrality in the inner surface of cellulose given by eqn (5) becomes:

$$V[\mathrm{Na}^+]_i + V[\mathrm{H}^+]_i - V[\mathrm{Cl}^-]_i - V[\mathrm{OH}^-]_i - [\mathrm{Cell-O}^-]_f - S = 0 \tag{16}$$

According to the Donnan membrane equilibrium theory, the activities of sodium chloride in both the phases may be assumed to be equal to each other:

$$[\mathrm{Na}^+]_s[\mathrm{Cl}^-]_s = [\mathrm{Na}^+]_i[\mathrm{Cl}^-]_i \tag{17}$$

When eqns (7), (10) and (12) are modified to be the corresponding equations in presence of sodium chloride, the equation corresponding to eqn (13) is given by:

$$V[\mathrm{Na}]_s^+ y - V[\mathrm{Cl}]_s/y - V[\mathrm{OH}^-]_s/y - \mathrm{G}/\{1 + K_w y/(K_a^C[\mathrm{OH}^-]_s)\} - S = 0 \tag{18}$$

This treatment, in the case of sodium chloride, is essentially the same as that of Sumner [1], although the method for obtaining the values of $[\mathrm{Na}^+]_i$ is different. This equation may be solved by the same procedure as that for eqn (13).

RESULTS AND DISCUSSION

Concentration of hydroxide ions in cellulose phase

As mentioned above (in the preceding two sections), the adsorption of sodium hydroxide on cellulose can be treated by Donnan membrane equilibrium theory [15, 16]. In this case, the carboxyl and cellulosate ions of cellulose correspond to the impermeable ions in the theory. Although in the original Donnan model, the concentrations of all the ions are uniform in both the phases, the carboxyl and cellulosate ions may exist on the surface of cellulose in the inner solution, and the distributions of other ions may be also heterogeneous as the result. Then, the mathematical equations can be described in terms of the mean concentrations of each species in the inner solution of the cellulose phase. Many workers [3–5, 18–20] have applied the Donnan equilibrium to the adsorption of anionic dyes on cellulose, a diffusely adsorbed model. But, the validity of treatment in the alkali adsorption on cellulose has been experimentally proved by Sumner [1], by taking all the ionic species in the system into consideration and being combined with the electroneutrality conditions [eqn (18)]. In addition to the concentration of $[\mathrm{OH}^-]_s$, such factors as the ionic strength of the external solution, the amount of fixed ionic groups in cellulose, and the dissociation of the hydroxyl groups of cellulose, have some effect on the alkaline adsorption.

The carboxyl group content in cellulose varies with the kind of cellulose, and their treatment as a textile fibre. The amount may be increased by various treatments, depending upon the conditions. In this paper, mercerized cotton with 10 meq. kg^{-1} of carboxyl groups is discussed (cf Table 1). The other values of parameters predetermined from the range of experimental values are listed in Table 1.

As given by eqn (2), the values of $[\mathrm{Cell{-}O}^-]_f$ depend on the concentration of hydroxide ions in the inner solution in cellulose. The relationships between $[\mathrm{OH}^-]_i$ and $[\mathrm{OH}^-]_s$ are, from eqns (4) and (6)

$$A = [\mathrm{OH}^-]_i/[\mathrm{OH}^-]_s = 1/y, \tag{19}$$

and are illustrated as a function of log $[\mathrm{OH}^-]_s$, and I in Fig. 1(a) for $S = 0.010$ eq. kg^{-1} and in Fig. 1(b) for $S = 0.100$ eq. kg^{-1}, respectively, by the numerical calculation of y(cf Section of calculation of $[\mathrm{Na}^+]_i$ in presence of sodium sulphate). In the case of $S = 0.010$ eq. kg^{-1} and log $[\mathrm{OH}^-]_s < -2.5$, the values of A are becomes 0.99 at $I = 2.0$, and are practically constant at $I \geqq 2.0$. With decrease in I, the values of A at log $[\mathrm{OH}^-]_s \risingdotseq -4$ decrease to 0.95 at $I = 0.4$, 0.90 at $I = 0.2$, and 0.80 at $I = 0.1$, respectively. The relationships between A and log $[\mathrm{OH}^-]_s$, in the case of larger values of S as an example for $S = 0.100$ eq. kg^{-1}, are shown in Fig. 1(b). The value of A at log $[\mathrm{OH}^-]_s < -2.5$ become 0.90 at $I = 2.0$, 0.57 at $I = 0.4$, and 0.17 at $I = 0.1$, respectively. The decrease in A at log $[\mathrm{OH}^-]_s < -2.5$ is negligible, although the constant values of A decrease with an increase in S and with a decrease in I (see below).

A gradual decrease in A at high alkalinity may be attributed to the co-ion exclusion by the dissociation of hydroxyl groups of cellulose. The exclusion

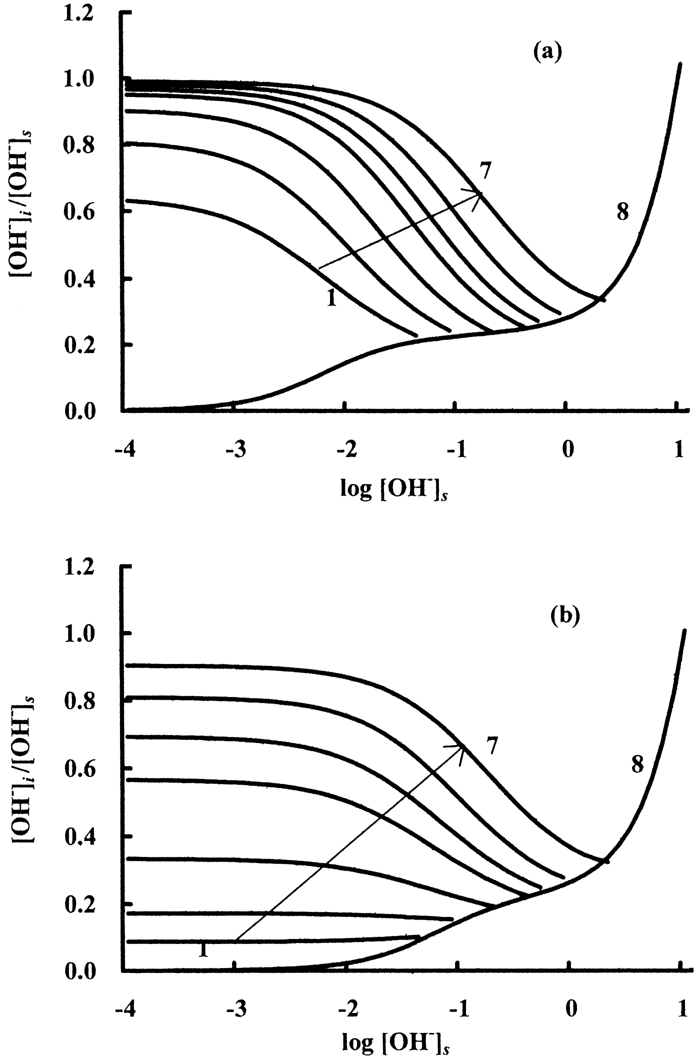

Fig. 1. (a) Relationships between $[OH^-]_i/[OH^-]_s$ $(=A)$ and log $[OH^-]_s$, for various values of I=0.05(1), 0.10(2), 0.20(3), 0.40(4), 0.60(5), 1.0(6), and 2.0(7) with 1:2-electrolyte for mercerized cotton in the case of S=0.010 eq. kg^{-1} at 25°C. Line 8 illustrates the same relationship where no electrolyte other than sodium hydroxide exists, and (b) the same relationships in the case of S=0.100 eq. kg^{-1}.

occurs also at low values of $[OH^-]_s$, with a decrease in I. However, the ionic repulsive interaction manifested by a decreasing tendency of A becomes prominent with an increase in S, and with a decrease in I. In the case of S=0.01 eq. kg^{-1}, the ionic strength in the dye bath at log $[OH^-]_s=-3$ should not be reduced below 0.2, to keep $A \geqq 0.90$, while in the case of

$S = 0.100$ eq. kg^{-1}, it should be maintained at $\geqq 2.0$ mol dm^{-3}. By use of only sodium hydroxide to adjust the pH of dye bath (i.e. without addition of neutral salt), the values of A do not rise to 0.23 at pH $\leqq 13$ (log $[OH^-]_s \leqq -1$, as shown by line 8 in Fig. 1(a) and (b).

In order to clarify the effects of I and S on A, and an abrupt decrease of A with a decrease in I, the relationships between A and I are shown in Fig. 2 for the cases of $S = 0$, 0.01, and 0.10 eq. kg^{-1} under the conditions of $[OH^-]_s = 10^{-2}$ and 10^{-3} mol dm^{-3}. With a decrease in I, the values of A where $S = 0.01$ mol kg^{-1} fall abruptly from $I = 0.3$ mol dm^{-3} at $[OH^-]_s = 10^{-3}$ mol dm^{-3}, and in case of $S = 0.100$ mol kg^{-1} from $I = 0.5$ mol kg^{-1}. At

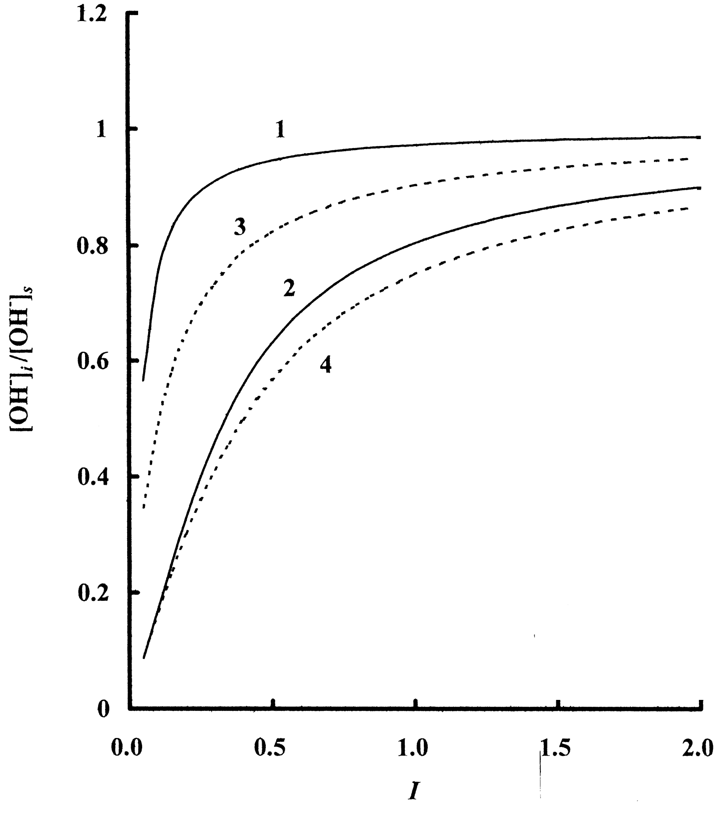

Fig. 2. Relationships between $[OH^-]_i/[OH^-]_s$ $(= A)$ and I (with 1:2-electrolyte as the neutral salt) for various values of S at the concentrations of $[OH^-]_s = 10^{-2}$ mol dm^{-3} (dotted line) and 10^{-3} mol dm^{-3} (solid line) for mercerized cotton at 25°C.

S eq. kg^{-1}	0.010	0.100
$[OH^-]_s = 0.001$ mol dm^{-3}	Line 1	Line 2
$[OH^-]_s = 0.010$ mol dm^{-3}	Line 3	Line 4

$[OH^-]_s = 10^{-2}$ mol dm^{-3}, the values of A fall with more larger ionic strengths. Thus, a decrease in I and an increase in the fixed ionic groups, or the progress of fixation of reactive dyes and the dissociation of hydroxyl groups of cellulose, result in the lowering of A, or that of the relative concentration of hydroxide ions in cellulose. Some leveling action may occur in the fixation process, although it is irreversible. Since, in practice, fixation occurs heterogeneously (for example, preferentially from the surface) the concentration of hydroxide ions is distributed unevenly in cellulose, accompanied by migration, to give a homogeneous distribution.

Relation between the ratios of [Cell-O$^-$]$_i$/[OH$^-$]$_i$ and [OH$^-$]$_i$

The hydroxyl groups of cellulose dissociate in an alkaline medium to give cellulosate ions. The relationship between the hydroxide ion concentration in the inner surface and the cellulosate ions can be represented as the acid dissociation curve shown by eqn (2). By use of the relation between $[OH^-]_i$ and $[OH^-]_s$, examined in the previous section, the relationships between $[\mathrm{Cell{-}O^-}]_f/V$ and log $[OH^-]_s$ can be drawn, as shown in Fig. 3(a). But, since the ions of $[\mathrm{Cell{-}O^-}]_f$ are fixed on cellulose, the relation between B and $[OH^-]_s$ is influenced by the Donnan equilibrium, combined with the electroneutrality conditions. Since the co-ion exclusion may occur with the progress of dissociation, the dissociation is retarded with a decrease in ionic strength. The right ends of lines 2 and 3 correspond to the limit of the corresponding ionic strength.

In order to express the ratio $B = [\mathrm{Cell{-}O^-}]_f/\mathrm{V}[OH^-]_i$ as a function of log $[OH^-]_s$, by combining eqs. (2) and (19), the ratio B is given by:

$$\begin{aligned} B &= [\mathrm{Cell{-}O^-}]_f/V[\mathrm{OH^-}]_i = [\mathrm{Cell - O^-}]_i/[\mathrm{OH^-}]_i = G/V(K_w/K_a^C + [\mathrm{OH^-}]_i) \\ &= G/V(K_w/K_a^C + [\mathrm{OH^-}]_s/y) \end{aligned} \tag{20}$$

A simple functional relation corresponding to the acid dissociation given by eqn (20) is shown as line 1 (in case of $y = 1$) in Fig. 3(b) for mercerized cotton, by use of the parameters in Table 1. Almost no effect is found on the plot with respect to the value of S, since $K_w/K_a^C \gg [\mathrm{OH^-}]_s$ in the weakly alkaline region. When $[\mathrm{OH^-}]_i \ll K_w/K_a^C$, i.e. in the weakly alkaline region, the value of B is equal to $(G/V)/(K_w/K_a^C)(= 17.4)$. Sumner [1] estimated this value to be 27, a higher value than that found in this present study. If 6.87×10^{-15} (a value for K_w at 20°C) is used as the value of K_w, as by Sumner [18], the value is estimated to be 27 by using the parameters for regenerated

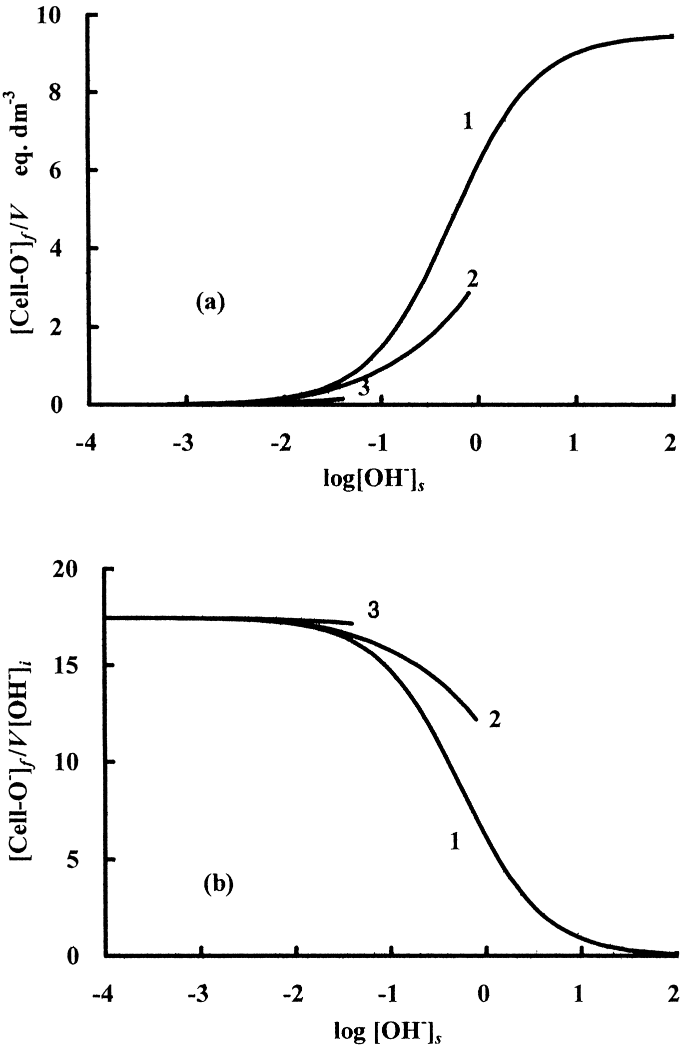

Fig. 3. (a) Relationships between $[\text{Cell–O}^-]_f/V$ and log $[\text{OH}^-]_s$ described by eqn (2) when $[\text{OH}^-]_i = [\text{OH}^-]_s$ (Line 1), and those for various values of ionic strengths (with 1:2-electrolyte as the neutral salt): 1.0 mol dm^{-3} (Line 2) and 0.01 mol dm^{-3} (Line 3) for mercerized cotton at 25°C, and (b) relationships between $[\text{Cell–O}^-]_f/V[\text{OH}^-]_i$ $(=B)$ and log $[\text{OH}^-]_s$ described by eqn (20) when $[\text{OH}^-]_i = [\text{OH}^-]_s$ (Line 1), and those for the same ionic strengths: 1.0 mol dm^{-3} (Line 2) and 0.01 mol dm^{-3} (Line 3) for mercerized cotton at 25°C.

cellulose in Table 1. The limiting values of B for various cellulose are listed in Table 1.

The values of B deviated to the upper side from line 1 at log $[\text{OH}^-]_s > -2$, as shown in Fig. 3(b) for $I = 1.0$ and 0.010 mol dm^{-3} (Lines 2 and 3). They show a mirror image relation between Fig. 3(a) and (b).

Relation between ratio of [Cell–O$^-$]$_f$/ V[OH$^-$]$_s$ and [OH$^-$]$_s$

The rations of C are given by multiplying A with B; the relationships between C and [OH$^-$]$_s$ are described by eqn (21):

$$\begin{aligned} C &= [\mathrm{Cell}-\mathrm{O}^-]_f/V[\mathrm{OH}^-]_s = [\mathrm{Cell}-\mathrm{O}^-]_i/[\mathrm{OH}^-]_s \\ &= G/V\{(K_w/K_a^C)y + [\mathrm{OH}^-]_s\} \end{aligned} \tag{21}$$

Since the sum, S, of the concentration of fixed anions in cellulose and the ionic strength are related to C, the relationships between C and log [OH$^-$]$_s$ are illustrated as a function of I in Fig. 4 in the case of $S = 0.010$ eq. kg^{-1}, and in Fig. 5 in the case of $S = 0.100$ eq. kg^{-1}, respectively. The values of [Cell–O$^-$]$_f$ are obtained by eqn (2) by using the values of [OH$^-$]$_i$ and y calculated by eqns (8) and (13), respectively.

The values of C were almost constant at log [OH$^-$]$_s < -2.5$ with changes in [OH$^-$]$_s$. The limiting value of C is 17.4, when [OH$^-$]$_i$ = [OH$^-$]$_s$ (cf. the previous section and Table 1). In the case of S = 0.010 eq. kg^{-1}, the values of C in the constant range are 17.2 at $I = 2.0$ mol dm^{-3}, 16.5 at $I = 0.4$ mol dm^{-3}, and 13.9 at $I = 0.1$ mol dm^{-3}, respectively. In the case of $S = 0.100$ eq. kg^{-1} the values of C are 15.7 at $I = 2.0$ mol dm^{-3}, 12.1 at $I = 0.6$ mol dm^{-3}, 9.9 at $I = 0.4$ mol dm^{-3}, and 3.0 at $I = 0.1$ mol dm^{-3}, respectively. Thus, the constant values of C at log[OH$^-$]$_s < -2.5$ decrease with a decrease in I and with an increase in S. This is because of the fact that the larger the concentration of the fixed anionic groups in cellulose, the more strongly the hydroxide ions may be excluded. With increase in pH, the values of A in the inner surface of cellulose decrease with a decrease in I, and with an increase in S, while a decrease in B occurs in the very high pH region.

In order to show more clearly how the values of C change with S, the relationships between C and S are illustrated in Fig. 6(a) at a constant concentration of [OH$^-$]$_s = 10^{-3}$ mol dm^{-3} and in Fig. 6(b) at a constant concentration of [OH$^-$]$_s = 10^{-2}$ mol dm^{-3}. If the fixation occurs homogeneously, Fig. 6(a) and (b) show that the inner pH, the concentration of cellulosate ion, or the pseudo-first order rate constant of the reaction decreases with the progress of fixation at the constant concentration, 10^{-2} and 10^{-3} mol dm^{-3}, respectively, of hydroxide ions in the dyebath. The values of C decrease considerably with an increase in S when $I < 1$, and remain almost constant when $I \geqq 2$, irrespective of S.

Differences between 1:1- and 1:2-electrolytes

The use of sodium chloride instead of sodium sulfate as the neutral salt need three times the concentration as that of sodium sulfate to adjust the solution

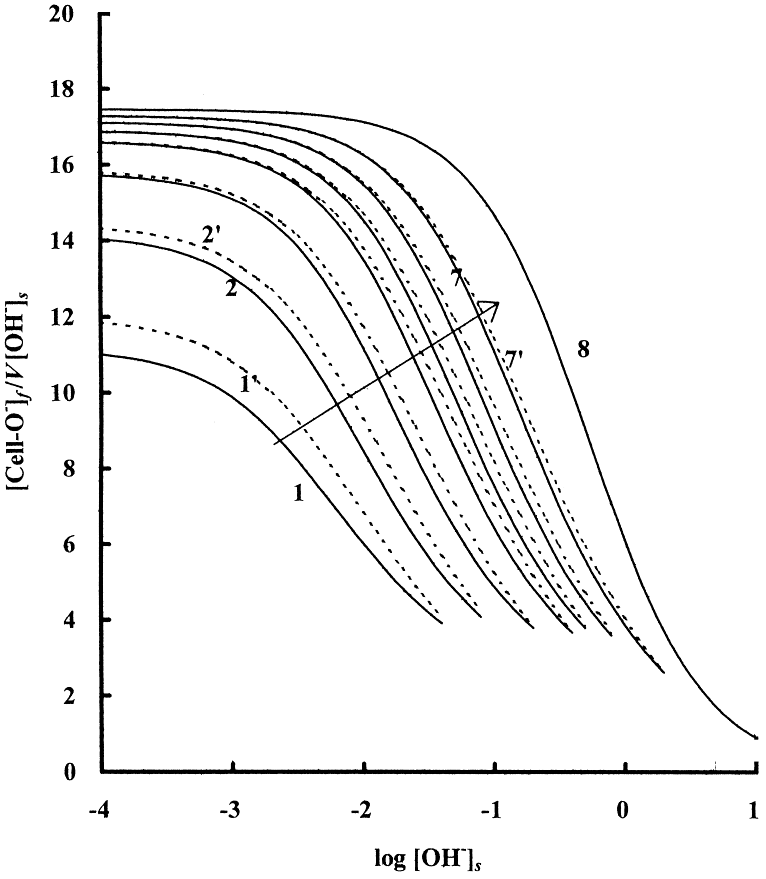

Fig. 4. Relationships between $[\text{Cell–O}^-]_f/V[\text{OH}^-]_s$ (= *C*) and log $[\text{OH}^-]_s$ for various values of I = 0.050(1), 0.10(2), 0.20(3), 0.40(4), 0.60(5), 1.0(6), and 2.0(7) for mercerized cotton in the case of S = 0.010 eq. kg^{-1} at 25°C. Sodium sulfate (solid line) or sodium chloride (dotted with dashed number) was used as the neutral salt to adjust the ionic strength. Line 8 illustrates the same relationship of eqn (20), when $[\text{OH}^-]_i$ equals $[\text{OH}^-]_s$, i.e., I≫1.0 mol dm^{-3}.

to the same ionic strength. Since mathematical equations are different from each other only in the factors for sulfate and chloride ions in eqs. (5) and (16), the ratios of $[\text{Cell–O}^-]_f/V[\text{OH}^-]_s$(= *C*) were calculated for 1:2- and 1:1-electrolytes as shown in Fig. 4(a) and (b). The functional relations for both the electrolytes is the same. The ratios for 1:1-electrolyte become larger than those for 1:2-electrolyte with an increase in the concentrations of hydroxide ions in the external solution, and of fixed anions in cellulose, and with a decrease in ionic strength, compared with those at the same concentrations of hydroxide ions or at the same pH.

Marshall [9–11] has shown a figure corresponding to Figs 3(b), 4 and 5 by use of sodium chloride. If he illustrated the relationships between B and log

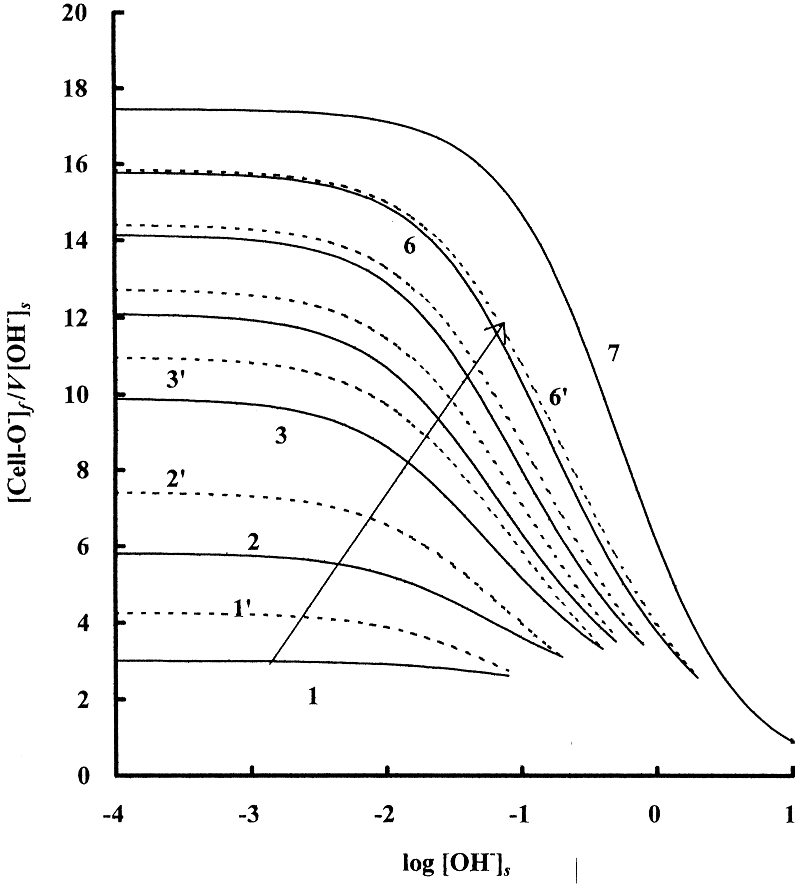

Fig. 5. Relationships between $[\text{Cell–O}^-]_f/V[\text{OH}^-]_{s-}(=\text{C})$ and $\log\,[\text{OH}^-]_s$ for various values of $I = 0.10(1)$, $0.20(2)$, $0.40(3)$, $0.60(4)$, $1.0(5)$, and $2.0(6)$ for mercerized cotton in the case of $S = 0.100$ eq. kg^{-1} at 25°C. Sodium sulfate (solid line) or sodium chloride (dotted with dashed number) was used as the neutral salt to adjust the ionic strength. Line 7 illustrates the same relationship of eqn (20), when $[\text{OH}^-]_i$ equals $[\text{OH}^-]_s$, i.e., $I \gg 1.0\,\text{mol}\,\text{dm}^{-3}$.

$[\text{OH}^-]_s$, which corresponds to Fig. 3(b), his results are erroneous. If he showed the relationships between C and $\log\,[\text{OH}^-]_s$, the relationships seems to contain some errors. As mentioned above, the ratios of C must become smaller than the limiting line described by eqn (20) (in case of $[\text{OH}^-]_i = [\text{OH}^-]_s$) from the low hydroxide ion concentration or low pH.

SUMMARY

The hydroxide ion concentrations in the inner solution of cellulose become smaller than those in the external solution due to co-ion exclusion by the

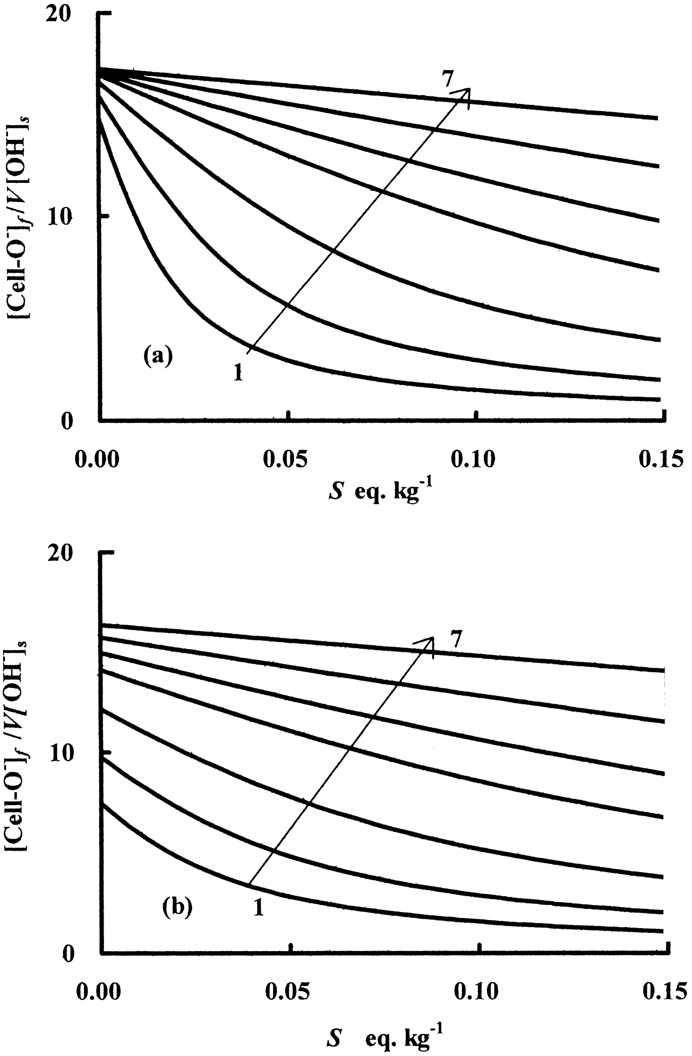

Fig. 6. (a) Relationships between $[\text{Cell–O}^-]_f/\text{V}[\text{OH}^-]_s$ ($= C$) and S at a constant concentration of $[\text{OH}^-]_s = 10^{-3}\,\text{mol dm}^{-3}$ for various values of I (with 1:2-electrolyte as the neutral salt): 0.05(1), 0.10(2), 0.20(3), 0.40(4), 0.60(5), 1.0(6), and 2.0(7) at 25°C, and (b) the same relationships at a constant concentration of $[\text{OH}^-]_s = 10^{-2}\,\text{mol dm}^{-3}$.

fixed anionic groups in cellulose. The tendency, therefore, increases with an increase in hydroxide ion concentrations and a decrease in the ionic strength in the external solution, and with an increase in the fixed ion concentration. This fact is important with respect to reactive dyeing with low salt addition.

In dyeing with low salt addition, the inner pH-values decrease with the progress of fixation. Simultaneous adsorption/fixation reactive dyeing (all-in method) should be avoided. Exhaustion dyeing in high yield is necessary before fixation, in order to give a high fixation ratio.

The present treatment can be applied to various cellulosics, whose values of parameters vary widely.

REFERENCES

1. Sumner, H. H., *Journal of the Society of Dyers and Colourists*, 1960, **76**, 672–678.
2. Neale, S. M., *Journal of the Textile Institute*, 1930, **21**, 225–230.
3. McGregor, R., *Textile Research Journal*, 1972, **42**, 536–552.
4. McGregor, R. and Ezuddin, K. H., *Journal of the Applied Polymer Science*, 1974, **18**, 629–632.
5. McGregor, R. and Ezuddin, K. H., *Textile Research Journal*, 1974, **44**, 43–44.
6. Sumner, H. H. and Vickerstaff, T., *Melliand Textilberichte*, 1961, **42**, 1161–1166.
7. Luttringer, J. P. and Dussy, P., *Melliand Textilberichte*, 1980, **62**, 84–94.
8. Morita, Z., Saito, T. and Motomura, H., *Journal of the Applied Polymer Science*, 1986, **32**, 3929–3939.
9. Marshall, W. J., *American Dyestuff Reporter*, 1969, **58**(17), 19–29.
10. Marshall, W. J., *Colourage Annual Ed.*, 1969, 87–99.
11. Marshall, W. J., *Textilveredlung*, 1969, **4**, 679–691.
12. Peters, R. H., Bleaching of cotton with sodium chlorite. In *Textile Chemistry, Vol. II, Impurities in Fibres; Purification of Fibres*, Ch. 12. Elsevier Publishing Co., Amsterdam, 1967, pp. 233–246.
13. Peters, R. H., Fine Structure. In *Textile Chemistry, Vol. I, The Chemistry of Fibres*, Ch. 14. Elsevier Publishing Co. Amsterdam, 1967, pp. 376–403.
14. Wadsworth, L. C. and Cuculo, J. A., Determination of accessibility and crystallinity of cellulose, In *Modified Cellulosics*. Ed. R. M. Rowell, and R. A. Young. Academic Press, New York, 1978, pp. 117–146.
15. Vickerstaff, T., Cellulose—dyeing equilibria with direct dyes. In *The Physical Chemistry of Dyeing*, 2nd edn., Ch. VII, Oliver and Boyd, London, 1954, pp. 191–256.
16. Guggenheim, E. A. and Turgeon, J. C., *Transactions of the Faraday Society*, 1955, **51**, 747–761.
17. Burdett, B. C., Physical chemistry essential to dyeing theory. In *The Theory of Coloration of Textiles*, 2nd edn., Ch. 1, ed. A. Johnson. The Society of Dyers and Colourists, Bradford, 1989, pp. 1–96.
18. Sumner, H. H., Thermodynamics of dye adsorption. In *The Theory of Coloration of Textiles*, 2nd edn., Ch. 4, ed. A. Johnson. The Society of Dyers and Colourists, Bradford, 1989, pp. 255–372.
19. Bae, S.-H., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1997, **34**, 37–55.
20. Motomura, H., Bae, S.-H. and Morita, Z., *Dyes and Pigments*, 1998, **36**, 61–77.