Dyes and Pigments, Vol. 36, No. 1, pp. 61–77, 1998

PII: S0143-7208(96)00126-X 0143-7208/97 $17.00+0.00

Effect of Anionic Groups in Cellulose on the Adsorption of Reactive Dyes on Cellulose

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(Received 12 October 1996; accepted 15 November 1996)

ABSTRACT

The adsorption of CI Reactive Red 120 and CI Direct Blue 1 on cellulose which was reactively-dyed with reactive dyes having six and eight sulfonate groups was examined at 80°C. Above a certain concentration of sodium sulfate, the same saturated adsorption on the dyed cellulose as that of undyed cellulose was observed. When all the dissociated groups were taken into consideration, the values of $-\Delta\mu^0$ *for the dyed cellulose were equal to that for the undyed cellulose within experimental errors. Thus, it was shown that only the anionic groups on cellulose had effect on the adsorption of anionic dyes on cellulose, whether it was dyed or not. How the adsorption of anionic dyes on cellulose on which the hydroxyl groups of cellulose and the dyes dissociated depended upon pH was examined by simulation. © 1997 Elsevier Science Ltd*

Keywords: Adsorption, reactive dyes, cellulose, anionic group, dissociation, hydroxyl group.

INTRODUCTION

Reactive dyes for cellulose have been designed to possess middle substantivity to attain high fixation yield and at the same time to allow removal of the unfixed species to give high wet fastness. However, some usual reactive dyes for cellulose have a low substantivity typical of acid dyes, while some dyes have the high substantivity of direct dyes [1]. Since the reaction of reactive

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dyes with cellulose is almost always carried out under alkaline conditions, both cellulose and the dyes used may be subjected to the influences of alkalinity. Usually, under such alkaline conditions, the adsorption of dyes on cellulose, the diffusion of dyes into and in cellulose, and reaction of the reactive groups with cellulose and water may occur simultaneously. At the same time, the functional (mainly hydroxyl) groups of the dyes on cellulose and in the dyebath, and such groups of cellulose, may dissociate depending upon the alkalinity. The unit processes of the reactive dyeing system under alkaline conditions, may be analyzed by their model or simulation experiments.

Thus, some unit processes of reactive dyeing, such as the adsorption on cellulose at high alkalinity of a model reactive dye which has no reactive group [2,3], the alkaline adsorption on cellulose [2], the adsorption of reactive dyes on reactively-dyed cellulose [4], the simultaneous diffusion and reaction for various reactive dyes [5–11], etc. have been studied.

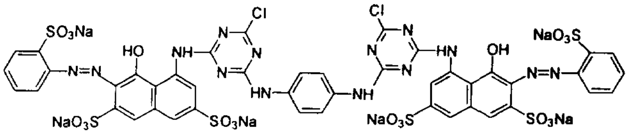
In the present paper, the adsorption of the anionic dyes, CI Reactive Red 120 and CI Direct Blue 1 on cellulose fixed with reactive dyes having six and eight sulfonate groups is investigated to elucidate the co-ion repulsion effect on the adsorption of anionic dyes. By a model experiment, whether or not the effects of sulfonate groups in the fixed dyes on the adsorption of anionic dyes can be quantitatively described by the Donnan adsorption theory combined with the principles of electroneutrality is examined. Additionally, whether or not the adsorption behavior of reactive dyes on reactively-dyed cellulose are changed with the amounts of fixed dyes is also investigated. How the dissociation of the functional groups of dyes influences the adsorption of the dye with an increase in alkalinity is then analyzed by simulation.

EXPERIMENTAL

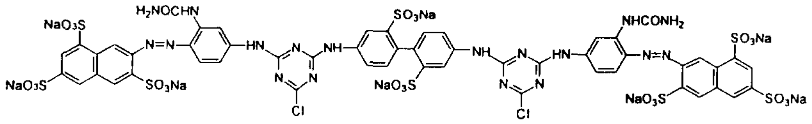
Materials

CI Reactive Red 120 and a monochlorotriazinyl (MCT) stilbene disazo dye (Yellow), which were supplied by Nippon Kayaku Co. Ltd. and CI Direct Blue 1, which was supplied by DyStar Japan Co. Ltd., were used. Their chemical structures and CI Generic and Constitution Numbers, if available, are shown below:

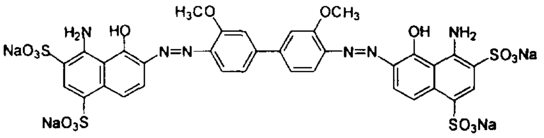
1) CI Reactive Red 120, CI 25810



2) A MCT stilbene disazo dye (Yellow)



3) CI Direct Blue 1, CI 24410



These dyes were purified by the previously reported method [1]. Cellulose film (Futamura Kagaku Kogyo K.K., #300) was used after scouring in boiling water for more than 2 h. The reactively-dyed cellophane (two levels of concentration) were prepared by immersing cellophane films in an alkaline solution (pH 11.2) for 2 h at 80°C after the equilibrium adsorption of Yellow or CI Reactive Red 120 from the neutral dyebath. After fixation, thorough washing with boiling water was carried out to remove the unfixed dye.

Procedure

The cellulose films were dyed at various concentrations of dye and salt at 80°C and pH 6.8 to attain the equilibrium adsorption. The concentration of dye adsorbed on the films at equilibrium and that of the residual dyebath after dyeing were determined from the absorbance using a V-550 spectrophotometer (Jasco Corp).

THEORETICAL

Symbols used

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

a_n	Activity of dye anions in the n^{th} phase
C	Amount of dyes determined on cellulose (mol kg^{-1})
C_f	Total concentration of dye on cellulose $= [D^{Z-}]_f + [D^{Z'-}]_f$(mol kg^{-1})

C_s	Total concentration of dye determined in the dyebath $= [D^{Z-}]_s + [D^{Z'-}]_s$ (mol dm^{-3})
$[Cell - COO^-]_f$	Concentration of carboxylato ions in cellulose (40 mmol kg^{-1})
$[Cell - D_1^{N-}]_f$	Concentration of fixed dye anion having N anionic groups in cellulose (mol kg^{-1})
$[Cell - O^-]_f$	Concentration of cellulosate ions in cellulose (mol kg^{-1})
$[D^{Z-}]_n$	Concentration of dye anion having Z anionic groups in the n^{th} phase (mol dm^{-3} for solution phase and mol kg^{-1} for solid phase, respectively)
G	Concentration of glucose unit (4.57 mol kg^{-1})
$[H^+]_n$	Concentration of hydrogen ions in the n^{th} phase (mol dm^{-3})
K_a^C	Acid dissociation constant of hydroxyl groups of cellulose (1.84×10^{-14} at 20°C)^{12}
K_a^D	Acid dissociation constant of functional groups of dyes
K_w	Ionic product of water (6.87×10^{-15} at 20°C)
$[Na^+]_n$	Concentration of sodium ions in the n^{th} phase (mol dm^{-3})
$[OH^-]_n$	Concentration of hydroxide ions in the n^{th} phase (mol dm^{-3})
R	Gas constant
$[SO_4^{2-}]_n$	Sum of the concentrations of sulfate and carbonate ions in the n^{th} phase (mol dm^{-3})
T	Absolute temperature (K)
V	Internal volume of cellulose (0.45 dm^3 kg^{-1})
Z	Charge number of dye anion (Total number of the sulfonic and carboxylic acid groups)
Z'	Charge number of dye anion after additional functional groups dissociated
$\Delta\mu^0_{D^{Z-}}$	Difference of the standard chemical potential of dye anions with Z charges between the fiber and dyebath phases (kJ mol^{-1}) (In text, suffix D^{Z-} is omitted)
μ^0_n	Chemical potential of dye anions in the n^{th} phase in the standards state

Values of $-\Delta\mu^0$ for reactive dye on reactively-dyed cellulose from aqueous sodium sulfate and carbonate

The differences, $-\Delta\mu^0$, between the chemical potential, $\mu_f{}^0$, of an anionic dye in its standard state on the fiber and the corresponding chemical potential, $\mu_s{}^0$, in its standard state in the dyebath, or so-called standard affinity, are given by eqn (1) [13, 14]:

$$-\Delta\mu^0_{D^{Z-}} = -(\mu^0_f - \mu^0_s) = RT\ln\frac{a_f}{a_s} = RT\ln\frac{[D^{Z-}]_f[\mathrm{Na}^+]^Z_f/V^{Z+1}}{[D^{Z-}]_s[\mathrm{Na}^+]^Z_s} \quad (1)$$

where the activity coefficient of all the ionic species is assumed to be unity and V is the internal volume.

Further dissociation of functional groups of dye in solution

If at an alkalinity the functional groups in the dye molecule dissociate, the dissociation equilibrium may be described as eqn (2):

$$D^{Z-} = D^{Z'-} + \mathrm{H}^+ \quad (2)$$

where the acid dissociation equilibrium (2) is defined by eqn (3).

$$K^D_a = \frac{[D^{Z'-}]_s[\mathrm{H}^+]_s}{[D^{Z-}]_s} \quad (3)$$

and usually,

$$Z' = Z + 1 \quad (4)$$

If the activity coefficients of all the species are assumed to be unity, the standard affinity of dye anions whose functional groups dissociated is given by eqn (5):

$$-\Delta\mu^0_{D^{Z'-}} = RT\ln\frac{[D^{Z'-}]_f[\mathrm{Na}^+]^{Z'}_f/V^{Z'+1}}{[D^{Z'-}]_s[\mathrm{Na}^+]^{Z'}_s} \quad (5)$$

In eqn (5), $[D^{Z'-}]_f$ and $[D^{Z'-}]_s$ cannot directly be determined, but their total concentrations, C_f and C_s can. This problem is discussed later.

Electroneutrality conditions

In water-swollen cellulose, the principles of electroneutrality may hold as follows:

$$V[\mathrm{Na}^+]_i + V[\mathrm{H}^+]_i - 2V[\mathrm{SO}_4^{2-}]_i - V[\mathrm{OH}^-]_i - Z[\mathrm{D}^{Z-}]_f - Z'[\mathrm{D}^{Z'-}]_f - [\mathrm{Cell-COO}^-]_f - [\mathrm{Cell-O}^-]_f - N[\mathrm{Cell-D}_1^{N-}]_f - N'[\mathrm{Cell-D}_1^{N'-}]_f = 0 \quad (6)$$

According to the Donnan membrane equilibrium theory, the activities of sodium sulfate, sodium carbonate, and sodium hydroxide in both the phases may be assumed to be equal to each other; viz., eqns (7) and (8).

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

$$[\mathrm{Na}^+]_s[\mathrm{OH}^-]_s = [\mathrm{Na}^+]_i[\mathrm{OH}^-]_i \tag{8}$$

where the concentration of carbonate ions is added to that of sulfate ion; thus, that of sulfate ion denotes the sum of their concentrations.

By combining eqn (6) with eqns (7) and (8) and rearranging, a cubic eqn (9) with $[\mathrm{Na}^+]_i$ is obtained:

$$\begin{aligned}(1 + K_W/[\mathrm{Na}^+]_s[\mathrm{OH}^-]_s)[\mathrm{Na}^+]_i^3 - V^{-1}\{Z[\mathrm{D}^{Z-}]_f + Z'[\mathrm{D}^{Z'-}]_f \\ +[\mathrm{Cell} - \mathrm{COO}^-]_f + [\mathrm{Cell} - \mathrm{O}^-]_f + N[\mathrm{Cell} - \mathrm{D}_1^{\mathrm{N}-}]_f \\ +N'[\mathrm{Cell} - \mathrm{D}_1^{\mathrm{N}'-}]_f\}[\mathrm{Na}^+]_i^2 - V[\mathrm{Na}^+]_s[\mathrm{OH}^-]_s[\mathrm{Na}^+]_i - 2[\mathrm{Na}^+]_s^2[\mathrm{SO}_4^{2-}]_s = 0\end{aligned} \tag{9}$$

In principle, the solution of the cubic eqn (9) gives $[\mathrm{Na}^+]_i$, but since , (9) contains several unknown parameters, no value of $[\mathrm{Na}^+]_i$ can be directly calculated.

RESULTS AND DISCUSSION

Adsorption of anionic dyes on reactive-dyed cellulose from the neutral dyebath

Adsorption behavior

As the first model experiments of the reactive dyeing system, the adsorption of anionic dyes on cellulose films with which CI Reactive Red 120 or Yellow reacted evenly was examined at 80°C. The adsorption isotherms of CI Direct Blue 1 and CI Reactive Red 120 on undyed and reactively-dyed cellulose films are shown in Figs 1–3. The amounts of dye adsorption on reactively-dyed cellulose were decreased by the repulsive effect of the sulfonate groups of the reactive dyes fixed previously. Thus, the larger the amounts of fixed dye and the lower the ionic strength, the decreasing tendency in the adsorption becomes more strongly apparent, compared with the case of undyed cellulose. Although the apparent substantivity of CI Direct Blue 1 was decreased with an increase in the amount of fixed dye, this dye showed the same saturation value on reactively-dyed cellulose as that on original cellulose, as shown in Figs 1 and 2. CI Reactive Red 120 showed the same behavior as that of CI Direct Blue 1 in the adsorption on cellulose which was fixed evenly with Yellow, as well as in the saturated adsorption (Fig. 3). CI Reactive Red 120 and Yellow had no different influence on the adsorption of CI Direct Blue 1 on cellulose reactively-dyed with them, in spite of the number of sulfonate groups.

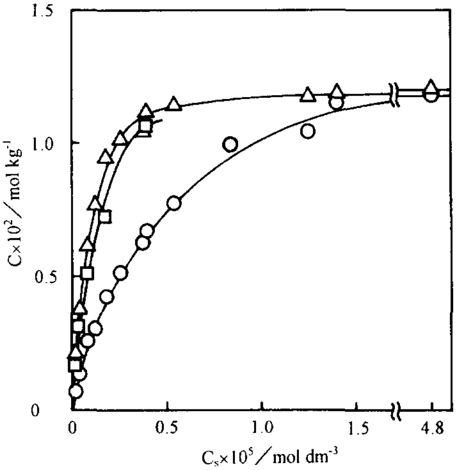


Fig. 1. Adsorption isotherms for CI Direct Blue 1 on undyed (△) and reactively-dyed cellulose films with CI Reactive Red 120 at concentrations of 0.00265 mol kg^{-1} (□) and 0.0163 mol kg^{-1} (○) at 80°C, pH 6.8 and 0.133 mol dm^{-3} of Na_2SO_4.

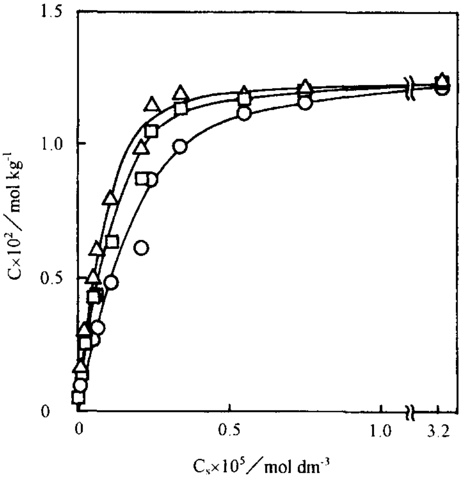


Fig. 2. Adsorption isotherms for CI Direct Blue 1 on undyed (△) and reactively-dyed cellulose films with Yellow at concentrations of 0.00219 mol kg^{-1} (□) and 0.00831 mol kg^{-1} (○) at 80°C, pH 6.8 and 0.133 mol dm^{-3} of Na_2SO_4.

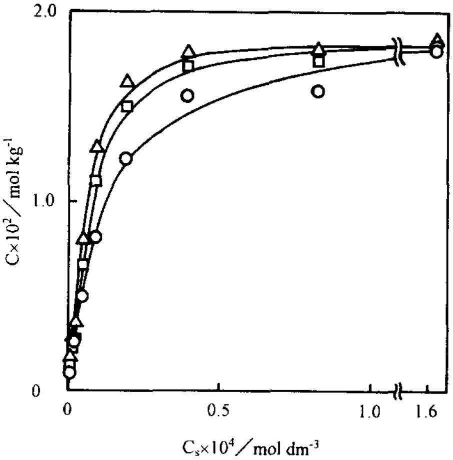


Fig. 3. Adsorption isotherms for CI Reactive Red 120 on undyed (△) and reactively-dyed cellulose films with Yellow at concentrations of 0.00219 mol kg^{-1} (□) and 0.00831 mol kg^{-1} (○) at 80°C, pH 6.8 and 0.333 mol dm^{-3} of Na_2SO_4.

Values of $-\Delta\mu^0$

As mentioned above, the values of $-\Delta\mu^0$ for these dyes on undyed and reactively-dyed cellulose can be estimated by eqn (1) on taking the effects of sulfonate groups of the fixed dyes into consideration. The relationships between $-\Delta\mu^0$ and C on undyed and reactively-dyed cellulose for CI Direct Blue 1 and CI Reactive Red 120 are shown in Figs 4 and 5, respectively. The values of $-\Delta\mu^0$ for these dyes were dependent upon the amount of the dyes adsorbed on cellulose, but independent on the amounts of CI Reactive Red 120 and Yellow which were fixed previously. Moreover, the changes in the values of $-\Delta\mu^0$ on reactively-dyed films with the dye concentrations were the same as those on undyed films. In the range of concentrations of salt and dye where saturated adsorption occurs, the decreasing tendency in the values of $-\Delta\mu^0$ for two dyes on original cellulose was observed to be similar to that on reactively-dyed cellulose.

The repulsive effects on sulfonate groups of the fixed dyes, therefore, could be completely described by the Donnan adsorption model where the electroneutrality was taken into consideration in both the cellulose and dyebath phases. Their influences did not depend upon the kinds of reactive dyes, but on the number of sulfonate groups in the fixed dyes, although the influences became larger with a decrease in the salt concentration in the dyebath. Moreover, within the experimental conditions examined, the amount of fixed dyes on cellulose had no influence on the values of $-\Delta\mu^0$ and the saturated adsorption values of anionic dyes.

Ionic interactions in the adsorption process must exist between dyes having several sulfonate groups, since an apparent decrease in the adsorption with an increase in the amount of fixed dyes was clearly found, while the values of $-\Delta\mu^0$ remained constant, as noted above. However, Harada *et al.* [4] investigated the levelling property of reactive dyes containing one and three sulfonate groups on undyed and reactively-dyed cotton, and reported

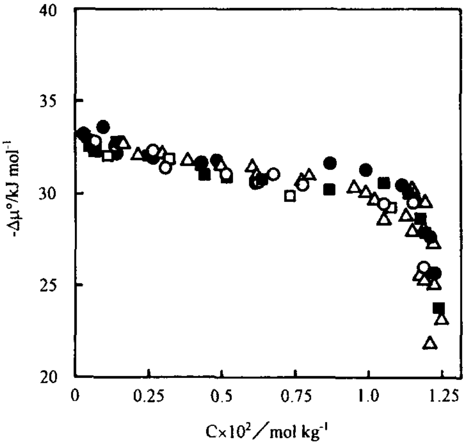


Fig. 4. Relationship between $-\Delta\mu^0$ and C for CI Direct Blue 1 on undyed (△) and reactively-dyed cellulose films with Yellow at concentrations of 0.00219 mol kg^{-1} (■) and 0.00831 mol kg^{-1} (●) and with CI Reactive Red 120 at concentrations of 0.00265 mol kg^{-1} (□) and 0.0163 mol kg^{-1} (○) at 80°C, pH 6.8 and at 0.133 mol dm^{-3} of Na_2SO_4.

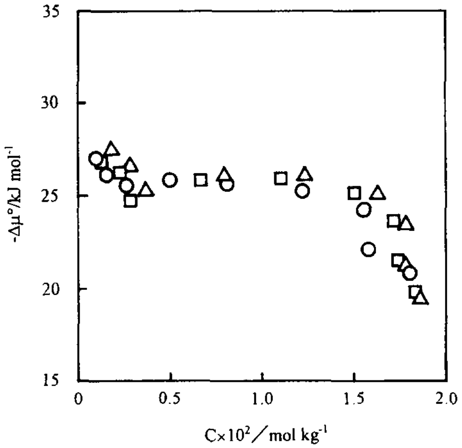


Fig. 5. Relationship between$-\Delta\mu^0$ and C for CI Reactive Red 120 on undyed (△) and reactively-dyed cellulose films with Yellow at concentrations of 0.00219 mol kg^{-1} (□) and 0.00831 mol kg^{-1} (○) at 80°C, pH 6.8 and at 0.133 mol dm^{-3} of Na_2SO_4.

that a dye with one sulfonate group showed no decrease in the apparent substantivity in the adsorption on reactively-dyed cotton. Other factors, such as swelling of reactively-dyed cellulose, may contribute to the adsorption.

Simulation of adsorption from the alkaline dyebath

The conclusions derived by the model adsorption experiments may be extended to analyze the adsorption of dyes under alkaline conditions. Since such functional groups in cellulose and dyes as hydroxyl and imino groups may dissociate under alkaline conditions, depending on the dissociation constants of the groups, the anionic character generated may influence the adsorption behavior of dyes as a result.

In fact, Sumner [2] investigated the adsorption of sodium hydroxide on cellulose and then the adsorption of a model anionic dye which had neither reactive nor dissociable functional groups on cellulose under alkaline conditions. Taking the dissociation of hydroxyl groups of cellulose into consideration, the values of $-\Delta\mu^0$ for the model dye on cellulose at high pH were found to be constant over a wide range of pH.

In a series of studies on the reaction accompanied by diffusion for various reactive dye ranges, the present authors [7, 8] reported some unusual behavior, such as a decrease of the surface concentration of reactive dye with an increase in pH, besides decrease in adsorption [2] due to the dissociation of cellulose hydroxyl groups, and a decrease of adsorption by alkali addition in batch-wise reactive dyeing [15].

Calculation of the amount of adsorption

In order to take into account the effects of dissociation of, for example, the hydroxyl groups of cellulose and the dye into consideration, and to analyze the adsorption of sodium hydroxide and the dissociated dyes on cellulose, the following assumptions were made:

(i) the values of $-\Delta\mu^0$ for the original and dissociated dyes are the same as each other, where the acid dissociation constant of the dye is K_a^D.
(ii) the ionic product of water in the inner surface of cellulose is the same as that of bulk water.
(iii) one of hydroxyl groups in each glucose unit dissociates in the inner surface of cellulose, whose acid dissociation constant is K_a^C.

On the basis of these assumptions and the given parameters, i.e. all the concentrations of species in the dyebath and all the values of $-\Delta\mu^0$ and acid dissociation constants, a simulation (or a calculation) of the adsorption of all the species on cellulose at pH 7-12 and 20°C, was carried out.

Calculation of $[\mathrm{Na}^+]_i$

a) $[D^{Z-}]_f$:

When the ratio of the concentrations of sodium ions in the two phases is defined by eqn (10):

$$\frac{[\mathrm{Na}^+]_i}{[\mathrm{Na}^+]_s} = y \tag{10}$$

from eqns (1), (3) and (5), the ratio of $[D^{Z-}]_f/[D^{Z'-}]_f$ in the fiber phase is given by eqn (11):

$$\frac{[D^{Z-}]_f}{[D^{Z'-}]_f} = \frac{[\mathrm{H}^+]_s}{K_a^D} y \cdot exp\left(\frac{-\Delta\mu^0_{D^{Z-}} + \Delta\mu^0_{D^{Z'-}}}{RT}\right) \tag{11}$$

Then, according to the assumption (i), $[D^{Z-}]_f$ is given by eqn (12):

$$[D^{Z-}]_f = \frac{[\mathrm{H}^+]_s [D^{Z'-}]_f}{K_a^D} y \tag{12}$$

On the other hand, assuming that $[\mathrm{Cell} - D_1^{N-}]_f = [\mathrm{Cell} - D_1^{N'-}]_f = 0$, $[D^{Z-}]_f$ is obtained from eqn (6), if $[\mathrm{H}^+]_i$ and $[\mathrm{SO}_4^{2-}]_i$ are known, obtained as below. Thus, from eqns (8) and (10), y is given by eqn (13):

$$y = \frac{[\mathrm{Na}^+]_i}{[\mathrm{Na}^+]_s} = \frac{[\mathrm{OH}^-]_s}{[\mathrm{OH}^-]_i} = \frac{K_w/[\mathrm{H}^+]_s}{K_w/[\mathrm{H}^+]_i} = \frac{[\mathrm{H}^+]_i}{[\mathrm{H}^+]_s} \tag{13}$$

where assumption (ii) was used in the derivation. When $[\mathrm{H}^+]_S$ is written as a function of $[\mathrm{OH}^-]_s$ and y by eqn (13) and similarly $[\mathrm{SO}_4^{2-}]_i$ as that of $[\mathrm{SO}_4^{2-}]_S$ and y by use of eqn (7), they can be written, respectively, as eqns (14) and (15)

$$[\mathrm{H}^+]_i = K_w y/[\mathrm{OH}^-]_s \tag{14}$$

$$[\mathrm{SO}_4^{2-}]_i = [\mathrm{SO}_4^{2-}]_s/y^2 \tag{15}$$

When $[D^{Z'-}]_f$ from eqn (12), eqn (4), and eqn (15) are introduced into eqn (6), by rearrangement, $[D^{Z-}]_f$ is then given by eqn (16):

$$[D^{Z-}]_f = \frac{V[\mathrm{Na}^+]_s y - 2V[\mathrm{SO}_4^{2-}]_s y^{-2} - [\mathrm{Cell} - \mathrm{COO}^-]_f - V[\mathrm{OH}^-]_s y^{-1} - [\mathrm{Cell} - \mathrm{O}^-]_f}{Z\left(1 + \frac{K_a^D}{[\mathrm{H}^+]_s} y^{-1}\right) + \frac{K_a^D}{[\mathrm{H}^+]_s} y^{-1}} \tag{16}$$

where the total concentration of sodium ions in the dyebath is given by eqn (17):

$$[\mathrm{Na}^+]_s = 2[\mathrm{SO}_4^{-2}]_s + ZC_s \tag{17}$$

In eqn (16), since the carboxyl groups of cellulose may be regarded as dissociating completely, the concentration is a known parameter. In this stage, the unknown parameters in eqn (16) are y and $[\mathrm{Cell} - \mathrm{O}^-]_f$, the calculations of which are noted below.

b) Calculation of y

From eqn (3) $[D^{Z-}]_s$ is rewritten as eqn (18):

$$[D^{Z-}]_s = \frac{C_s[\mathrm{H}^+]_s}{K_a^D + [\mathrm{H}^+]_s} \tag{18}$$

and then, from eqn (1), $[D^{Z-}]_f$ is given by eqn (19):

$$[D^{Z-}]_f = V\left(\frac{[\mathrm{Na}^+]_s}{[\mathrm{Na}^+]_f/V}\right)^Z [D^{Z-}]_s \exp\left(-\frac{\Delta\mu^O_{D^{Z-}}}{RT}\right) \tag{19}$$

By introducing eqns (13) and (18) into eqn (19), eqn (19) becomes eqn (20):

$$[D^{Z-}]_f = Vy^{-Z}\frac{C_s[\mathrm{H}^+]_s}{K_a^D + [\mathrm{H}^+]_s}\exp\left(-\frac{\Delta\mu^0_{D^{Z-}}}{RT}\right) \tag{20}$$

On inserting the value of $-\Delta\mu^0$ determined previously, the values of y can be numerically determined so that eqn (20) = eqn (16), into which an equation for $[\mathrm{Cell-O^-}]_f$ as a function of $[\mathrm{OH^-}]_S$ and y (i.e. eqn (24), see below) was introduced. The values of $[D^{Z-}]_f$ can be then obtained, since the value of $[\mathrm{Cell-O^-}]_f$ can simultaneously be determined by the calculation.

Thus, using this calculation, the value of y can be determined, from which that of $[\mathrm{Na^+}]_i$ can be obtained using eqns (10) and (17) by use of the value of $[\mathrm{Cell-O^-}]_f$ mentioned below.

Calculation of C_f

When the value of y is determined, the value of $[D^{Z-}]_f$ is also obtained. Since $[D^{Z'-}]_f$ is obtained from eqn (12), C_f as a function of $[\mathrm{H^+}]_s$ and y is given by eqn (21):

$$C_f = [D^{Z-}]_f + [D^{Z'-}]_f = [D^{Z-}]_f\left(1 + \frac{K_a^D}{[\mathrm{H^+}]_s y}\right) \tag{21}$$

This functional relation has been already used in the derivation of eqn (16).

When $[\mathrm{H^+}]_s < K_a^D$, the corresponding equations for $[D^{Z'-}]_f$ of eqn (16) and eqn (20) can be written instead of $[D^{Z-}]_f$, from which the value of $[D^{Z'-}]_f$ can be obtained by the same procedure.

Calculation of $[\mathrm{Cell-O^-}]_f$

According to assumption (iii), the acid dissociation equilibrium for cellulose hydroxyl groups in the inner solution of cellulose is defined by eqn (22):

$$K_a^C = \frac{[\mathrm{Cell-O^-}]_i[\mathrm{H^+}]_i}{V^{-1}[\mathrm{Cell-OH}]_f} \tag{22}$$

After rearrangement, the concentration of cellulosate ion is given by eqn (23):

$$[\mathrm{Cell-O^-}]_f = \frac{G \cdot K_a^C}{[\mathrm{H^+}]_i + K_a^C} \tag{23}$$

Substituting eqn (14) for $[\mathrm{H^+}]_i$ in eqn (23) gives eqn (24):

$$[\mathrm{Cell-O^-}]_f = \frac{G \cdot K_a^C}{yK_w/[\mathrm{OH^-}]_s + K_a^C} \tag{24}$$

Since at $\mathrm{pH} \geqq 7$, the value of $[\mathrm{Cell-COO^-}]_f$ may well be regarded as being constant due to complete dissociation, the ratios of $[\mathrm{Cell-O^-}]_f/[\mathrm{Cell-COO^-}]_f$ can be obtained from eqn (24).

Since Neale [12] determined the value of K_a^C only at 20°C, the other constants measured at the same temperature can be used, and the values of $[\mathrm{Cell-O^-}]_f$ are calculated as the values at 20°C. In order to estimate a value at different temperature, the determination of K_a^C and K_a^D at such temperatures is required. For example, if the value of $[\mathrm{Cell-O^-}]_i/[\mathrm{OH^-}]_S$ at 80°C is calculated with values of K_a^C at 20°C and K_W at 80°C, it becomes less than 10.

Analysis of a decrease in the adsorption with an increase in pH

Dissociation of cellulose hydroxyl groups

Since the adsorption of the active species of reactive dyes on cellulose could not be experimentally determined under alkaline conditions, a simulation experiment on the adsorption of hypothetical dyes on cellulose was made. The effect that the dissociation of the cellulose hydroxyl groups had on the adsorption of the dyes on cellulose was initially analyzed.

For dyes whose $-\Delta\mu^0$ values are 5 and 30 kJ mol^{-1} (the values of $-\Delta\mu^0$ for reactive dyes may be in this range) [1], the values of C_f were calculated as a function of pH from eqn (21) at 20°C. The dyebath conditions and the dye properties are shown in the figure caption of Fig. 6. The results for the adsorption of dyes whose $pK_a^D \gg 14$ are illustrated as curves II_1 and II_3 in Fig. 6. In order to illustrate the results in the same ordinate, a dyebath of a very low concentration was used for a dye having high affinity. Since dyes with a value of $pK_a^D \gg 14$ do not dissociate, the value of $[D^{Z-}]_s/C_s$ (cf. eqn (18)) is always unity. A decrease in the adsorption for the dyes occurs due to the dissociation of hydroxyl groups of cellulose only above pH 10.5. These phenomena are discussed below.

In order to represent an increase of cellulosate ions, the ratios of $[\mathrm{Cell-O^-}]_f/[\mathrm{Cell-COO^-}]_f$ were calculated by eqn (24) as a function of pH, and are shown as curves: III_1 at $I=0.133$ mol dm^{-3} and III_3 at $I=1.00$ mol dm^{-3}. Since $[\mathrm{Cell-O^-}]_f$ depends also upon the ionic strength of the dyebath, a decrease in the adsorption at higher ionic strength occurs at higher pH than that at lower ionic strength. Above pH 10.5, the values of $[D^{Z-}]_f$ and the ratios of $[\mathrm{Cell-O^-}]_f/[\mathrm{Cell-COO^-}]_f$ were inversely changed relative to each other with increase in pH. The adsorptions of anionic dyes were inversely proportional to the amounts of dissociation with an increase in pH, implying good reciprocal relationships between II_1 and III_1 and between II_3 and III_3. Thus, below pH 10.5, there may be no influence on the adsorption of a reactive dye by the effects of dissociation of the cellulose hydroxyl

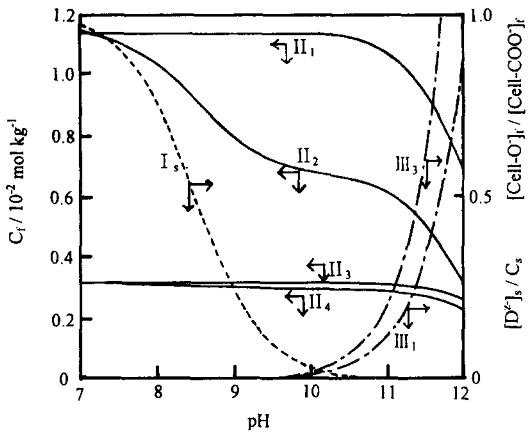


Fig. 6. Simulation of adsorption of hypothetical dyes ($Z = 2$) on cellulose. Symbols used for illustration in figure and the values of parameters used for the calculation.

Dye	*Dye properties*		*Dyebath cond.*		$[D^{Z-}]_s/C_s$	C_f*4	$[Cell-O^-]_f/[Cell-COO^-]_f$
	$-\Delta\mu^{0}$*1	pK_a^D	C_S*2	I*3			
1	30	$\gg$14	4×10^{-7}	0.1333	(1.0)	II$_1$	III$_1$
2	30	8.5			I$_S$	II$_2$	
3	5	$\gg$14	1×10^{-3}	1.000	(1.0)	II$_3$	III$_3$
4	5	8.5			I$_S$	II$_4$	

*1kJ mol^{-1}; *2mol dm^{-3}; *3Ionic strength of dyebath (mol dm^{-3}); *4mol kg^{-1}

groups on the adsorption. If reactive dyes have no additional dissociation groups other than sulfonate groups, the adsorption on cellulose may show no pH dependence below pH 10.5. Thus, usual reactive dyeing under alkaline conditions should be performed at pH 10.5, or at pH a little higher than 10.5.

Dissociation of functional groups in dyes

In order to demonstrate a decrease in the adsorption in weakly alkaline region with an increase in pH [7, 8], the effect of dissociation of such functional groups in the dye as the hydroxyl groups of the H-acid residue was analyzed. Assuming that pK_a^D of the hydroxyl groups is 8.5, and according to the assumption (i), the ratios $[D^{Z-}]_s/C_s$ in the dyebath were calculated as a function of pH by eqn (18) and are shown as curve I$_S$. The total adsorption of both the species, C_f, calculated for dyes with $-\Delta\mu^0$ values of 30 and 5 kJ mol^{-1} by eqn (21), is shown as curves II$_2$ and II$_4$, respectively, in Fig. 6. When the value of $-\Delta\mu^0$ is high, the influence of the additional dissociation of the dye on the adsorption is evident, as shown by II_2, even though the dissociated species have the same affinity. In cases of dyes with low affinity, only a gradual decrease in the adsorption is observed, as shown by II_4.

When the dissociation groups, such as the hydroxyl groups in the dye, are dissociated, the co-planarity of the dye may be lost, and the assumption of the same affinity may become invalid, although similar simulation can be made if the value of $-\Delta\mu^0$ for the dissociated species is known. As the result, the decreasing tendency of adsorption may become larger. Moreover, after the fixation, the dissociation or the increase in the anionic character of the dye in cellulose may have a larger influence on the adsorption of the dye. Reactive dyes need to possess larger values of pK_a^D in order to attain a high fixation ratio, which may be also improved by "sophistication" of the dyeing procedure.

A decrease in the adsorption with increasing pH in weakly alkaline region, which was found for CI Reactive Orange 1, Red 1, Red 2, and Red 8 (dichlorotriazinyl dyes) [7, 8] may be attributed to this additional dissociation of these dyes, because they have considerable substantivity to cellulose, as noted above.

SUMMARY

The adsorption of CI Reactive Red 120 and CI Direct Blue 1 on cellulose reactively-dyed previously with reactive dyes having six or eight sulfonate groups showed not only the same saturated adsorption, but also the same affinity, as those on undyed cellulose. Although the apparent substantivity was decreased due to the ionic repulsive interaction with increase in the amount of fixed dye, the adsorption was described by the Donnan membrane equilibrium theory combined with the electroneutrality in both the phases. With increase in the pH of the dye-bath, the hydroxyl groups of cellulose and dyes may dissociate to reduce the adsorption of reactive dyes. A decrease due to the dissociation of cellulose occurs at $\mathrm{pH} > 10.5$, and that due to the dissociation of specific dyes may occur in the weakly alkaline region.

An apparent decrease in the adsorption of reactive dyes on cellulose occurred by the ionic repulsive interaction of the dissociated groups at $\mathrm{pH} \geqq pK_a^C$ or $pK_a^D - 1.5$, but their affinity to cellulose was constant.

ACKNOWLEDGEMENT

The authors thank Nippon Kayaku Co. Ltd. for their cooperation in the preparation of this paper.

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