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Adsorption Behavior of Reactive Dyes on Cellulose

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ABSTRACT

The adsorption of three anionic dyes (CI Reactive Red 120, a monochlorotriazinyl red dye (Red E), and CI Direct Blue 1) on cellulose was investigated from a neutral dyebath at 80°C over a wide concentration range of sodium sulfate. Because of the apparent low substantivity, no accurate adsorption was determined at low electrolyte concentrations, where a higher apparent substantivity of the dyes was observed. The standard chemical potential differences between the cellulose and solution phases, or the standard affinity, $-\Delta\mu^0$*, for these dyes were calculated on the basis of the Donnan equilibrium model. CI Reactive Red 120 and CI Direct Blue 1 showed saturation in the adsorption isotherm, while Red E had a likeness to the other dyes when a high salt concentration was used. The substantivity of several reactive dye ranges is discussed, comparing them with the present results.* *© 1997 Elsevier Science Ltd*

1. INTRODUCTION

With the recent increase in world-wide environmental issues, the environmental protection regulations for textile processing and the ecological demands on the dyeing system are growing.[1–5] Reactive dyeing, especially at deep depths, is far from the required levels. In the development of reactive dyes, ICI introduced the Procion H-E dye range for exhaust dyeing and the Procion SP dyes for printing as reactive dyes of the second generation.[6–9] Procion H-E and SP dyes show about 90%, and more than 90%, fixation in dyeing and printing, respectively. However, even in the case of Procion H-E dyes, the addition of large amounts of neutral salts to the dyebath is necessary to attain high fixation. Removal of neutral salts from waste water is required to avoid river pollution. In order to decrease the required effluent treatment, and to attain as high a fixation as possible, reactive dyes should exhibit high fixation. However, reactive dyes have been considered in terms of not having too high a substantivity in order to remove unreacted dye after fixation. They have been regarded as requiring a balance in substantivity between high fixation and high wet fastness.

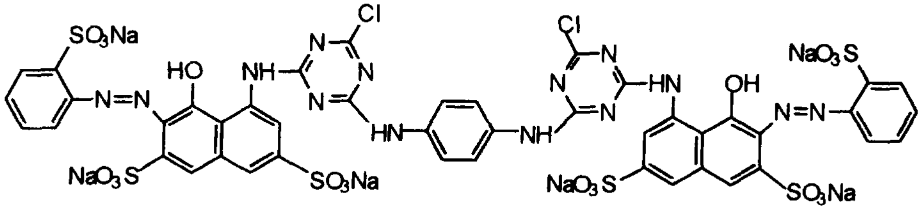
In the present paper, in order to analyze the importance of substantivity in the fixation of reactive dyes, the adsorption behavior of CI Reactive Red 120, a typical monochlorotriazinyl (MCT) reactive dye with high fixation for exhaust dyeing, and of a more usual MCT dye for exhaust dyeing on cellulose, is investigated over a wide range of electrolyte concentrations, because the dye has considerable substantivity to cellulose. As a representative of direct dyes, the adsorption of CI Direct Blue 1 on cellulose is also examined for comparison with that of reactive dyes. The substantivity of usual reactive dye ranges is also discussed, for comparison with the results reported herewith.

2. EXPERIMENTAL

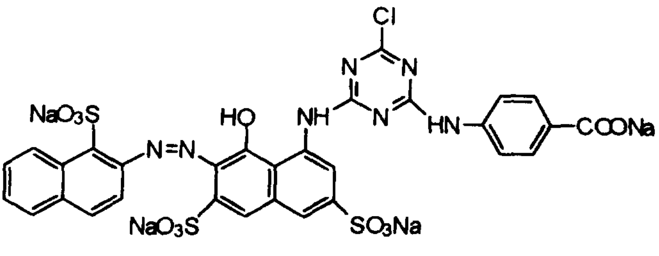
2.1. Materials

The dyes used were CI Reactive Red 120 and a MCT monoazo red dye (Red E), supplied by Nippon Kayaku Co. Ltd, and CI Direct Blue 1, supplied formerly by DyStar Japan Co. Ltd. Their chemical structures and CI Generic and Constitution Numbers, where available, are as follows:

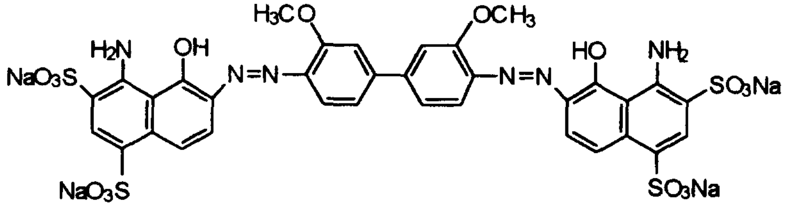
(1) CI Reactive Red 120, CI 25810



(2) A MCT monoazo dye (Red E)



(3) CI Direct Blue 1, CI 24410



CI Direct Blue 1 was purified by the Robinson and Mills method[10] and the MCT dyes used by using an organic solvent[11] to avoid hydrolysis. Cellulose film (Futamura Kagaku Kogyo K.K., #300) was used after scouring in boiling water for more than 2 h.

2.2. Procedure

The equilibrium adsorption of these dyes on cellulose was determined by immersing pieces of cellulose film (*ca.* 2×3 cm^2) in a dyebath (500 dm^{-3}) containing sodium sulfate over a wide range of concentrations at 80°C and pH 6.8. Reactive and direct dyes took 4 and 3 days, respectively, to attain the equilibrium adsorption. After dyeing, the dyed films were quickly and strongly pressed between filter papers to remove excess water and then dried between papers on which a weight was placed. The concentrations of dye adsorbed on the films at equilibrium and the dye concentrations in the dyebath after the equilibrium adsorption were determined by measurements of optical density. The optical density was measured using a V-550 spectrophotometer (Jasco Corp.). The optical density of high adsorption was checked by extracting the dye on cellophane with aqueous 50% dimethylformamide.

2.3. Calculation of the values for $\Delta\mu^0$

2.3.1. *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*-phase
C	amount of dyes determined on cellulose (mol kg^{-1})
C_s	concentration of dye determined in the dyebath (mol dm^{-3})
$[\text{Cell-COO}^-]_f$	amount of carboxylato groups in cellulose (40 mmol kg^{-1})
$[D^{Z-}]_n$	concentration of dye anion in the *n*-phase (mol dm^{-3} for solution phase and mol kg^{-1} for solid phase, respectively)
$[Na^+]_n$	concentration of sodium cations in the *n*-phase (mol dm^{-3})

R	gas constant
$[SO_4^{2-}]_n$	concentration of sulfate ions in the n-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 sulfonic and carboxylic acid groups)
$\Delta\mu^0$	difference in standard chemical potential of dye anions between the fiber and dyebath phases (kJ mol^{-1})
μ_n^0	chemical potential of dye anions in the n-phase in the standard state

2.3.2. Adsorption of dyes from aqueous sodium sulfate

The differences, $-\Delta\mu^0$, between the chemical potential, μ_f^0, of the dye in its standard state on the fiber and the corresponding chemical potential, μ_s^0, in its standard state in the dyebath, or so-called standard affinity, are given by equation 1:[12,13]

$$-\Delta\mu^0 = -(\mu_f^0 - \mu_s^0) = RT\ln\frac{a_f}{a_s} = RT\ln\frac{[D^{Z-}]_f[Na^+]_f^Z/V^{Z+1}}{[D^{Z-}]_s[Na^+]_s^Z} \tag{1}$$

where the activity coefficient of all the ionic species is assumed to be unity and V is the internal volume whose value is 0.45 dm^3 kg^{-1}.

According to the Donnan membrane equilibrium theory, the activity of permeable sodium and sulfate ions in both the solution and fiber phases should be equal (eqn 2):

$$[Na^+]_s^2[SO_4^{2-}]_s = [Na^+]_i^2[SO_4^{2-}]_i. \tag{2}$$

On the other hand, the principle of electroneutrality in the inner surface solution phase of the fiber should hold for all the ionic species as shown in equation 3:

$$V[Na^+]_i - 2V[SO_4^{2-}]_i - Z[D^{Z-}]_f - [Cell - COO^-]_f = 0 \tag{3}$$

following McGregor's analysis of the effect of the carboxyl groups in cellulose on the adsorption of anionic dyes.[14,15] The effect of the dissociation of the carboxyl groups should be taken into consideration even in the neutral region, since they dissociate completely, while the effect of the dissociation of hydroxyl groups on the adsorption of reactive dyes may be neglected, the latter effects in the highly alkaline region being reported by Sumner.[16]

In the present case, the concentration of all the ionic species in the solution can be simply determined by the dyeing recipe. But the concentration of sodium ions in the inner surface of cellulose must be calculated by use of equations 2 and 3. Thus, by combining the equations the cubic equation 4 with $[\mathrm{Na}]_i$ is obtained:

$$[\mathrm{Na}^+]_i^3 - V^{-1}(Z[\mathrm{D}^{Z-}]_f + [\mathrm{Cell} - \mathrm{COO}^-]_f)[\mathrm{Na}^+]_i^2 - 2[\mathrm{Na}^+]_s^2[\mathrm{SO}_4^{2-}]_s = 0. \tag{4}$$

The third term on the left-hand side of equation 4 is a constant which is determined experimentally. Since equation 4 contains no term of first order, the discriminant for equation 4 shows that this equation has only one positive real root within the experimental conditions used. This equation can be solved analytically by the Cardano method and the root was obtained using a computer program.

3. RESULTS AND DISCUSSION

3.1. Equilibrium adsorption from the neutral dyebath

3.1.1. CI Reactive Red 120

The adsorption behavior of reactive dyes has been studied by Sumner[16] by use of a model reactive dye. He showed that irrespective of the apparent decrease in the adsorption with increase in the alkalinity of the dyebath, the values of $\Delta\mu^0$ for the dye were kept constant, if the adsorption of alkali on cellulose was taken into consideration. The adsorption isotherms of CI Reactive Red 120 on cellulose were determined at 80°C from the neutral dyebath containing various concentrations of sodium sulfate, as shown in Fig. 1. The experimental results under typical experimental conditions are also shown in Table 1 as an example. As anticipated from the fact that the dye has six sulfonic groups in its molecule, the adsorption of CI Red 120 was strongly influenced by neutral salt added to the dyebath, i.e. a high salt sensitivity.[17]

The dye was little adsorbed at low $\mathrm{Na_2SO_4}$ concentrations, below 0.010 mol dm^{-3}, and a variation in the adsorption behavior began to appear at the concentration ≥ 0.10 mol dm^{-3}, and the saturated adsorption phenomenon appeared at the concentration ≥ 0.27 mol dm^{-3} (cf. Section 3.2). This behavior becomes clear when the values of $-\Delta\mu^0$ for this dye were calculated by equation 1. They are shown as the relationships between $-\Delta\mu^0$ and C/C_s for this dye in Fig. 2, and the values under experimental conditions are shown in Table 1. At intermediate salt concentrations, the values of $-\Delta\mu^0$ were almost constant over all the range of dye concentrations used, and at high salt concentrations they deviated downwards at high concentrations of dye and at small values of C/C_s (cf. Section 3.3). The latter behavior corresponds to the saturated adsorption.

At low salt concentration (≤ 0.033 mol dm^{-3}), on the other hand, they deviated upwards at smaller values of C/C_s, showing an increase in the apparent substantivity. Daruwalla and D'Silva[18] observed an increase in the standard affinity for CI Direct Blue 1 on cellulose at a low concentration of dye in the dyebath. If this increase was illustrated in Fig. 2, the deviation may appear at large values of C/C_s, i.e. a different phenomenon observed in this present study to that found by the above authors.

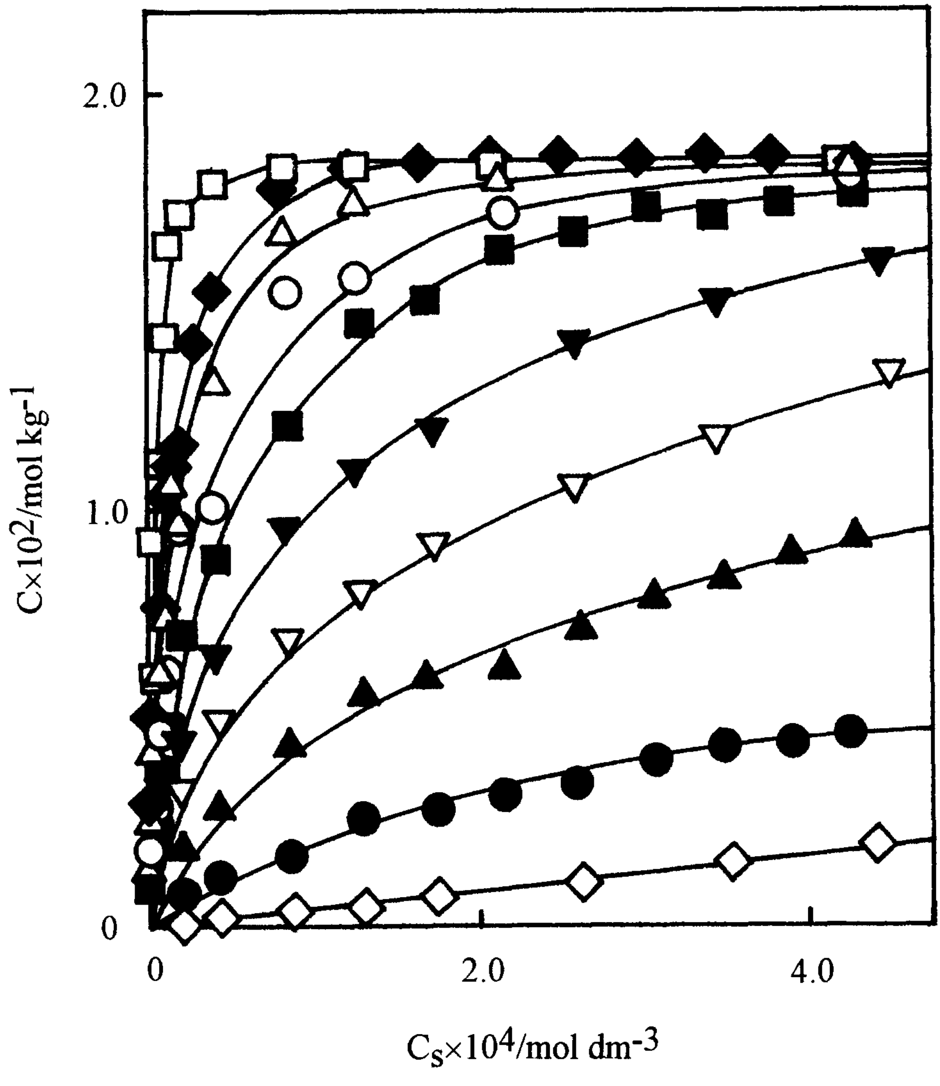


Fig. 1. Adsorption isotherms for CI Reactive Red 120 on cellulose film at 80°C, pH 6.8 and at various concentrations of Na_2SO_4: 0.00833 (◇), 0.0167 (●), 0.0333 (▲), 0.0667 (▽), 0.100 (▼), 0.133 (■), 0.200 (○), 0.267 (△), 0.333 (◆), 0.533 (□) mol dm^{-3}.

Since the upward deviation in the value of $-\Delta\mu^0$ in the present study was observed at high concentrations of dye in the dyebath or at low values of C/C_s, this phenomenon may be attributed to the inclusion of dye in the dye solution imbibed by cellulose (cf. Section 3.3). CI Reactive Red 120 has too low a substantivity at a low concentration of salt to neglect the dye in solution absorbed by cellulose.

3.1.2. Red E

In the case of Red E, whose substantivity to cellulose was lower than that of CI Red 120, the salt effect on the adsorption was also observed. At a high salt concentration (0.53 mol dm^{-3}), Red E was not adsorbed further at high concentration with increase in the dye concentration in the dyebath. Judging from the shape of the adsorption isotherms, a saturation phenomenon seemed to appear in the adsorption at high sodium sulfate concentration, as shown in Table 2 and Fig. 3. Extrapolation of the Langmuir plots to the infinite concentration of the dyebath gave a value nearly equal to the saturation value. This value is then shown as the saturation value in Table 3.

The relationships between $-\Delta\mu^0$ and C/C_s for this dye are illustrated in Fig. 4, showing the same pattern as that of CI Reactive Red 120. The downward deviation of $-\Delta\mu^0$ at high dye concentrations in the dyebath was confirmed by the additional experiments with very high concentration of dye,

TABLE 1

Equilibrium Adsorption and Values of $-\Delta\mu^0$ for CI Reactive Red 120 on Cellulose under Dyebath Conditions of 80°C, pH 6.8, and 0.333 mol dm^{-3} Na_2SO_4

$C_s \times 10^4$ mol dm^{-3}	$[Na^+]_s$ mol dm^{-3}	$C \times 10^2$ mol kg^{-1}	$[Na^+]_i$ mol dm^{-3}	$-\Delta\mu^0$ kJ mol^{-1}
0.00995	0.667	0.166	0.706	25.1
0.0151	0.667	0.294	0.712	25.7
0.0357	0.667	0.497	0.723	25.0
0.0759	0.667	0.760	0.736	24.4
0.116	0.667	1.04	0.752	24.4
0.161	0.667	1.11	0.756	23.7
0.198	0.667	1.15	0.758	23.3
0.291	0.667	1.40	0.772	23.1
0.397	0.667	1.52	0.779	22.6
0.804	0.667	1.77	0.795	21.3
1.24	0.667	1.81	0.797	20.1
1.66	0.668	1.83	0.799	19.3
2.08	0.668	1.85	0.800	18.7
2.52	0.668	1.85	0.800	18.1
2.99	0.668	1.84	0.800	17.6
3.39	0.669	1.85	0.801	17.3
3.79	0.669	1.85	0.801	16.9
4.30	0.669	1.84	0.800	16.5

as shown in Fig. 4 and Table 2. At low concentration of sodium sulfate (0.0083 mol dm^{-3}), Red E also has an apparent high substantivity due to the inclusion of dye solution.

3.1.3. CI Direct Blue 1

In order to compare the adsorption behavior of reactive dyes with that of typical direct dyes, the adsorption of CI Direct Blue 1 on cellulose was also determined over a wide range of salt concentrations. Figures 5 and 6 show

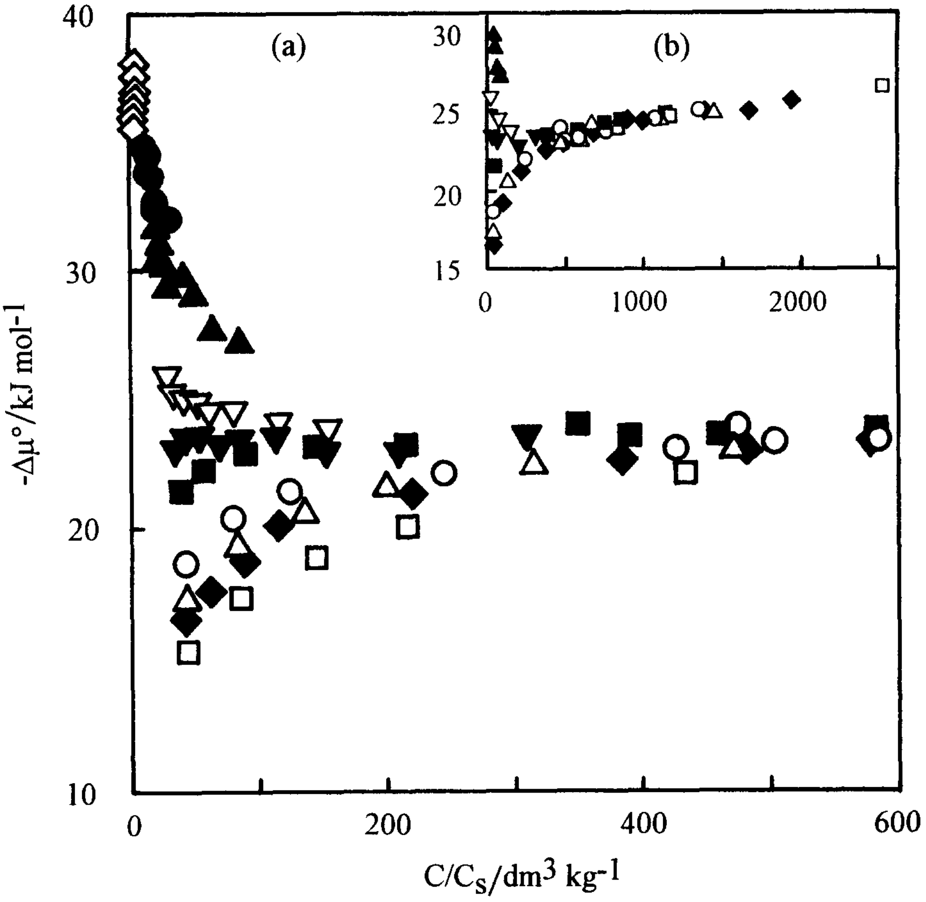


Fig. 2. (a) Relationship between $-\Delta\mu^0$ and C/C_s for CI Reactive Red 120 on cellulose film at 80°C from the dyebath containing various concentrations of Na_2SO_4: 0.00833 (◇), 0.0167 (●), 0.0333 (▲), 0.0667 (▽), 0.100 (▼), 0.133 (■), 0.200 (○), 0.267 (△), 0.333 (◆), 0.533 (□) mol dm^{-3}. (b) The same relationship between them at larger values of C/C_s (the plots at smaller values of C/C_s are roughly shown).

that the adsorption behavior of this dye was almost similar to that of CI Reactive Red 120 (the apparent high substantivity at Na_2SO_4 concentrations -0.05 mol dm^{-3} and the saturated adsorption at a salt concentration of 0.13 mol dm^{-3}) although the relationship between the values of $-\Delta\mu^0$ and C is illustrated in Fig. 6. The behavior is the same as that observed by Daruwalla *et al.*,[18,19] but the fact that CI Direct Blue 1 has a high substantivity at a low dye concentration was not found in the present study.

3.2. Saturation phenomena of adsorption

As mentioned above, the saturation phenomena were observed in the adsorption on cellulose for all the dyes examined at relatively high salt concentrations. The phenomena for direct dyes in the adsorption on cellulose have been reported by some workers.[18-20] The saturation values for some direct dyes, together with the results of the present experiment, are summarized in Tables 3 and 4. The saturation values of these dyes on cellophane are in the order of 0.01–0.03 mol kg^{-1}. Their values for direct dyes are within a very narrow range on the same substrate, except for CI Direct Blue 1 (Table 4).

TABLE 2

Equilibrium Adsorption and Values of $-\Delta\mu^0$ for Red E on Cellulose under Dyebath Conditions of 80°C, pH 6.8, and at the Concentrations of 0.333 and 0.533 mol dm^{-3} Na_2SO_4

$C_s \times 10^4$ mol dm^{-3}	$[Na^+]_s$ mol dm^{-3}	$C \times 10^2$ mol kg^{-1}	$[Na^+]_i$ mol dm^{-3}	$-\Delta\mu^0$ kJ mol^{-1}
0.169	0.667	0.227	0.703_2	17.4
0.326	0.667	0.402	0.708	17.2
0.683	0.667	0.694	0.715	16.7
1.45	0.667	1.18	0.728	16.3
2.07	0.667	1.77	0.744	16.7
2.84	0.668	2.01	0.751	16.2
4.36	0.668	2.16	0.755	15.2
5.61	0.669	2.57	0.767	15.2
6.97	0.669	2.70	0.771	14.7
0.156	1.07	0.378	1.11	18.9
0.305	1.07	0.639	1.11	18.5
0.645	1.07	1.03	1.12	17.8
1.41	1.07	1.65	1.14	17.1
2.09	1.07	2.00	1.15	16.6
2.75	1.07	2.32	1.16	16.3
4.15	1.07	2.83	1.17	15.8
5.43	1.07	2.96	1.17	15.2
7.07	1.07	2.91	1.17	14.3
10.51	1.07	2.96	1.20	13.5
22.08	1.08	3.00	1.21	11.3

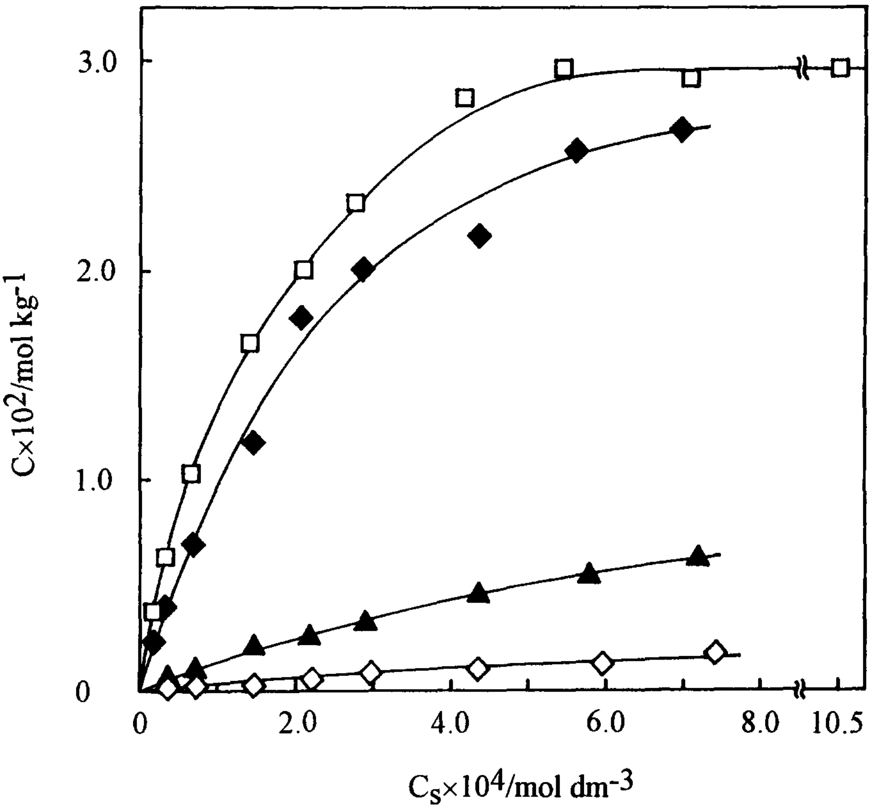


Fig. 3. Adsorption isotherms for Red E on cellulose film at 80°C and pH 6.8 and at various concentrations of Na_2SO_4: 0.00833 (◇), 0.0333 (▲), 0.333 (◆), 0.533 (□) mol dm^{-3}.

TABLE 3

Values of $-\Delta\mu^0$ and Saturation Values for the Three Dyes on Cellulose Determined at 80°C and pH 6.8

Dyes (molecular weight)	*Values of $-\Delta\mu^0$*		*Saturation values*	
	kJ mol^{-1}	*Concentration range used*	*10^{-2} mol kg^{-1}*	*Na_2SO_4 Conc.*
CI Reactive Red 120 (1540)	23.8 ± 1.1	Na_2SO_4: 0.100–0.533 mol dm^{-3} Dye conc. $\leq 1.66 \times 10^{-2}$ mol kg^{-1}	1.84 ± 0.01	≥ 0.267 mol dm^{-3}
Red E (900)	17.1 ± 1.1	Na_2SO_4: 0.033–0.533 mol dm^{-3} Dye conc. $\leq 2.83 \times 10^{-2}$ mol kg^{-1}	2.96 ± 0.04	0.533 mol dm^{-3}
CI Direct Blue 1 (992)	32.1 ± 0.8	Na_2SO_4: 0.033–0.133 mol dm^{-3} Dye conc. $\leq 0.95 \times 10^{-2}$ mol kg–1	1.21	0.133 mol dm^{-3}

According to Daruwalla *et al.*,[18,19] the saturation values of direct dyes on cellulose are independent of the temperature and of the concentration of salt, although they were dependent on the type of substrate. The saturation values of a specific dye on different substrates were proportional to their inner surface areas. The present result for CI Reactive Red 120 shows that the saturation values on cellulose were also independent of the concentration of sodium sulfate (Fig. 1 and Table 3). Daruwalla and D'Silva[18] observed, for a series of direct dyes, a decrease in the saturation values on cellulose with an increase in the number of sulfonic acid groups in the molecule. They considered that the size of dye molecules is the primary factor with respect to the saturation values. The present results, however, imply that there are other factors in the dye structure which determine the saturation values, since CI Direct Blue 1 has smaller values than CI Reactive Red 120. The saturation values may be changed by appropriate molecular design, as exemplified by the Procion H-E dyes with high values, and by the Procion SP dyes with low values.

Comparing the saturation behavior of three dyes examined, CI Direct Blue 1 showed saturated adsorption at relatively low salt concentration, CI Reactive Red 120 at an intermediate concentration, and Red E at the highest concentration, as expected from the order of substantivity, although the order of saturation values was the reverse, probably by chance.

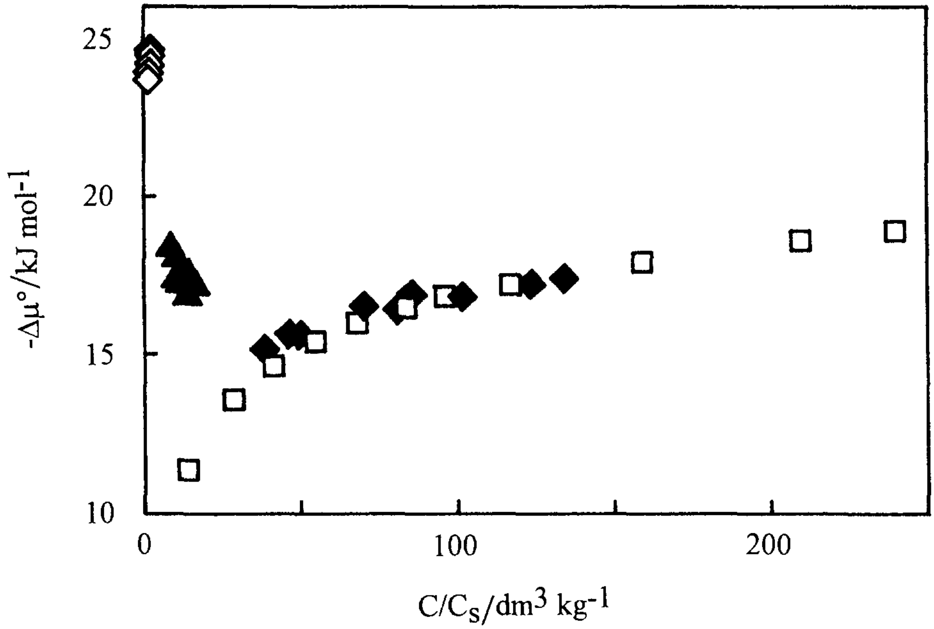


Fig. 4. Relationship between $-\Delta\mu^0$ and C/C_s for Red E on cellulose film at 80°C and pH 6.8 and at various concentrations of Na_2SO_4: 0.00833 (◇), 0.0333 (▲), 0.333 (◆), 0.533 (□) mol dm^{-3}.

The saturation values estimated from the adsorption isotherms were conjectured to correspond roughly to the completion of monomolecular adsorption on the inner surface of the substrate.[18,19] Near to, and above, the saturation values, intermolecular repulsive interaction between dye anions adsorbed on the inner surface of cellulose becomes appreciable in restricting further adsorption (a decrease in the value of $-\Delta\mu^0$). An increase in the intermolecular attractive interaction between adsorbed species may promote such aggregation as stacking, if the dyes possess such aggregation tendencies, although no saturation may appear in this case. However, such a phenomenon was not observed in the adsorption of anionic dyes on cellulose. The fact that no further adsorption occurs over the saturation value indicates a monomolecular adsorption of these dyes on cellulose, and not a multilayer one. No difference in the adsorption behavior for dyes with different aggregation properties was observed in the present study. These results, together

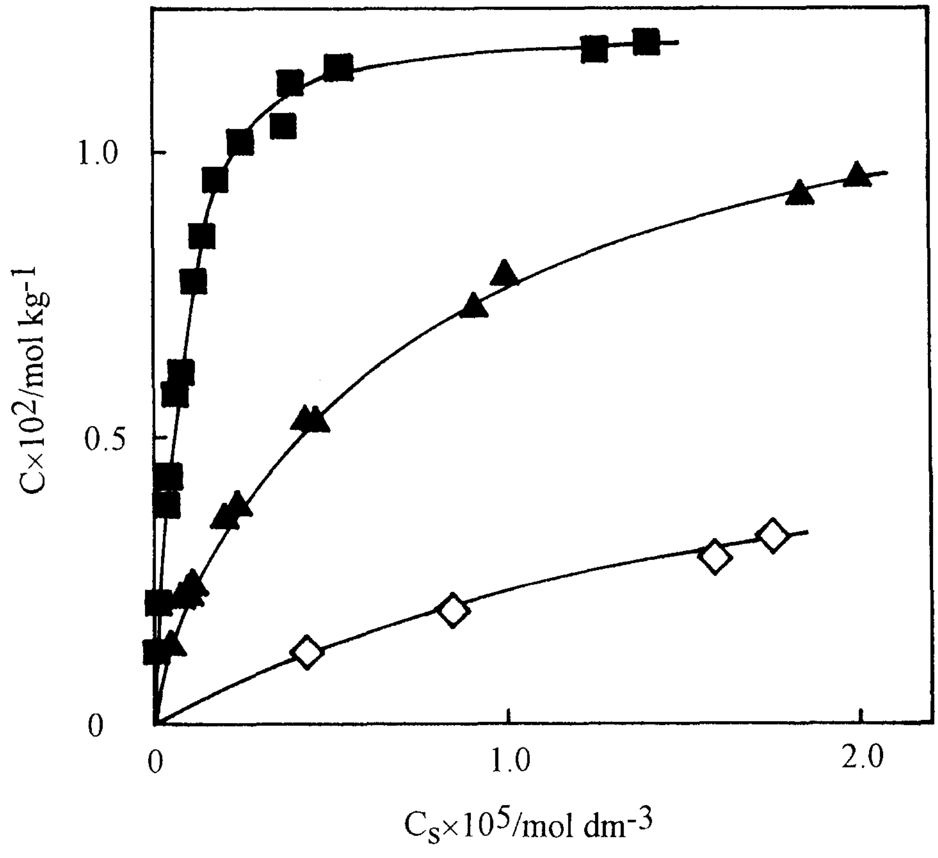


Fig. 5. Adsorption isotherms for CI Direct Blue 1 on cellulose film at 80°C and pH 6.8 and at various concentrations of Na_2SO_4: 0.00833 (◇), 0.0333 (▲), 0.133 (■) mol dm^{-3}.

with those by Daruwalla *et al.*,[18,19] therefore seem to suggest the monomolecular adsorption of these dyes on cellulose.

3.3. Values of standard chemical potential differences, $-\Delta\mu^0$

The values of $-\Delta\mu^0$ for CI Reactive Red 120, Red E, and CI Direct Blue 1, calculated from equation 1, are shown in Figs 2, 4 and 6, as the relationships between these values and the C/C_s ratios, or the relationships between the values of $-\Delta\mu^0$ and C, and in Table 1 (CI Reactive Red 120) and Table 2 (Red E) as examples.

The mean values of $-\Delta\mu^0$ for these dyes are summarized in Table 3. The mean value of $-\Delta\mu^0$ for CI Reactive Red 120 was calculated from the equilibrium adsorption at 80°C, except for the case of salt concentrations

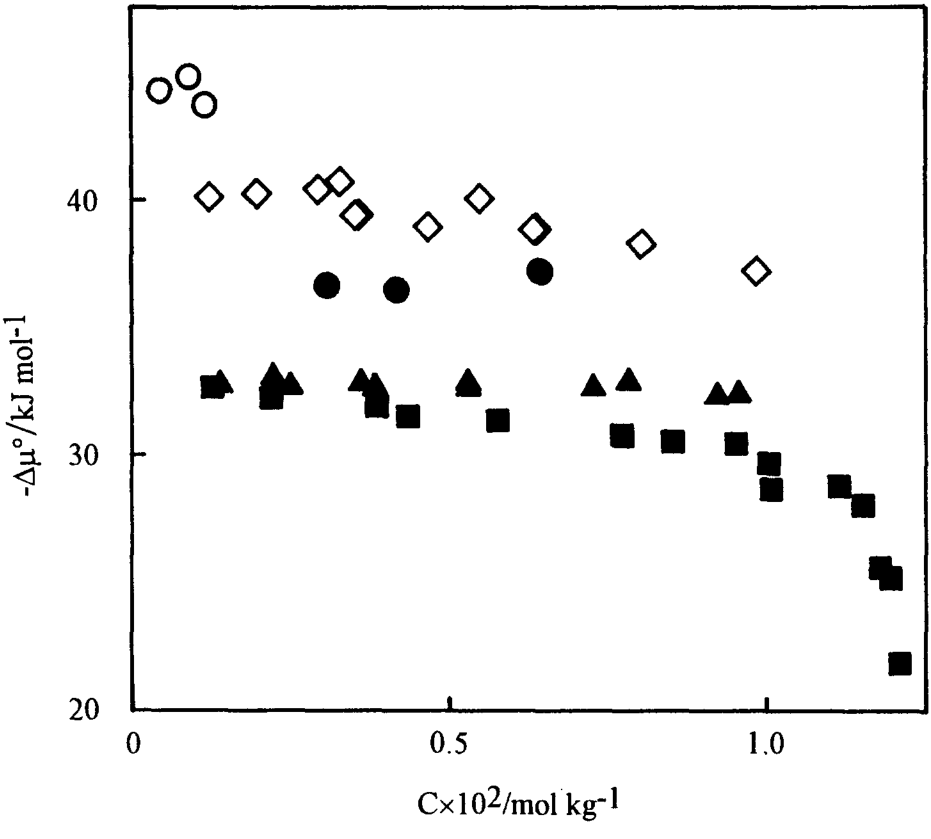


Fig. 6. Relationship between $-\Delta\mu^0$ and C for CI Direct Blue 1 on cellulose film at 80°C and pH 6.8 and at various concentrations of Na_2SO_4: 0.00417 (○), 0.00833 (◇), 0.0167 (●), 0.0333 (▲), 0.133 (■) mol dm^{-3}.

490.067 mol dm^{-3} and of dye concentrations on cellulose > 1.7 mol kg^{-1}, where the effect of saturation needs to be considered. The range of concentrations of salt in solution and that of dyes on cellulose, which were used for the calculation, are also shown in Table 3. The dye anions in the fiber phase, whose concentrations were experimentally determined, may be comprised of the species in the adsorbed state on the inner surface of cellulose, ones which are distributed diffusely from the inner surface within the double layer in the inner solution of cellulose, ones in the outside of the double layer in cellulose, and the ones in the superfluous solution on the surface of the cellulose. It is not possible to estimate the precise concentrations of each term. However, the contribution of the last two terms to the

TABLE 4

Saturation Values and Values of $-\Delta\mu^0$ for Some Anionic Dyes on Cellulose

Dyes	*Substrate*	*Saturation values*			*Values of* $\Delta\mu^0$ *kJ* mol^{-1} *(Temp./°C)*	*Reference*
		mol kg^{-1}	*Temp.* (°C)	*Salt used (conc./mol* dm^{-3}*)*		
CI Reactive Red 120	Cellophane	0.0184	80	Na_2SO_4 ($\geq$0.27)	23.8 (80)	This study
Red E	Cellophane	0.0296	80	Na_2SO_4 (0.53)	17.1 (80)	This study
CI Direct Blue 1	Cellophane	0.121	80	Na_2SO_4 (0.13)	32.1 (80)	This study
	Cotton	0.0101	60–90	NaCl (0.02)	32.1 (60)	18
	Viscose rayon	0.0151	60–90	NaCl (0.02)	32.4 (60)	18
	Cupra rayon	0.0181	60–90	NaCl (0.02)	30.5 (60)	18
CI Direct Yellow 12	Cotton	0.0177	60–90	NaCl (0.01)	16.3 (60)	18
	Viscose rayon	0.0265	60–90	NaCl (0.01)	16.2 (60)	18
	Cupra rayon	0.0309	60–90	NaCl (0.01)	15.6 (60)	18
CI Direct Red 28	Cotton	0.0187	60–90	NaCl (0.01)	25.2 (90)	18
	Viscose rayon	0.0273	60–90	NaCl (0.01)	26.5 (90)	18
	Cupra rayon	0.0316	60–90	NaCl (0.01)	24.1 (90)	18
CI Direct Red 2	Cotton	0.018	60–90	NaCl (0.086)	37.8 (80)	19
CI Direct Red 7	Cotton	0.0199	60–90	NaCl (0.086)	36.5 (80)	19
CI Direct Red 61	Cotton	0.0196	60–90	NaCl (0.086)	39.5 (80)	19

concentration in the fiber phase may be negligible when the ratio of C/C_s is very large or the apparent substantivity of dye is high, where the precise value of the adsorption can be determined. In the reverse case, where the ratio of C/C_s is relatively small, since the contribution of imbibed external solution to the concentration of dye in the fiber becomes considerable, the higher value of $-\Delta\mu^0$ than that of the mean value may be estimated (cf. Section 3.1.1).

Except for the large deviation of $-\Delta\mu^0$ from the mean value, small decreases in the values with an increase in the concentrations of dye on cellulose were noticed at higher concentrations of sodium sulfate in the dyebath besides the experimental scattering. Thus, the values of $-\Delta\mu^0$ showed a dye concentration dependence under conditions of constant electrolyte concentration. But, when the range of dye concentrations on cellulose is relatively narrow, as in the case of lower salt concentration (0.033 mol dm^{-3}), a smaller deviation of $-\Delta\mu^0$ was observed, as shown in Figs 4 and 6, although the ranges of concentration in the dyebath were similar to each other.

Strictly speaking, the concentrations of dye and sodium ions must be expressed by the activity in a mixture of sodium sulfate and the dye in both the phases. Since the concentration of dye ions is low compared with that of sodium sulfate, the activity of dye ions in sodium sulfate solution may be expressed by the trace activity concept[21] and those of the dye and sulfate ions have the common counter ion effect of sodium ions.[21,22] But, the dye, sulfate, and sodium ions in the inner solution phase of cellulose may be diffusely distributed. The amount of adsorption does not correspond to a definite concentration of dye anions in the fiber phase. A considerable part of this amount may exist in the adsorbed state, and the other part in the inner solution of cellulose. The anions in the inner solution consist of the diffusely distributed parts inside and outside the diffuse double layer in the fiber phase and of the part in the imbibed external solution. The activity of their ions, therefore, can be neither theoretically nor experimentally determined, although some workers avoided this difficulty by use of a Langmuir-type adsorption mechanism.[18,19] Other workers tried to modify the concentration dependence of the value of $-\Delta\mu^0$ by a change in the volume term.[23-5]

In this paper, all the activity coefficients are assumed to be unity and the values of $-\Delta\mu^0$ were calculated as the mean ones within experimental error. But from the fact that a larger concentration dependence or larger deviation of $-\Delta\mu^0$ was observed when the range of C/C_s was wider (and vice versa), the deviation of $-\Delta\mu^0$ may be attributed mainly to the deviation of the activity coefficients in the fiber phase. The fact that no clear effect of salt concentration on the activity of dye ions was observed may imply their cancellation between both the phases. The above problems remain to be solved.

3.4. Comparison of substantivity among reactive dyes

As a measure of substantivity, the values of $-\Delta\mu^0$ to cellulose for anionic dyes, given by equation 1, are of great importance. From previous results reported by the present authors,[26–30] the values for several reactive dye ranges were calculated as shown in Table 5. The values of $-\Delta\mu^0$ were estimated from the values of surface concentration, C_0, in the cylindrical film roll method by assuming that the kind of electrolyte had no influence on the C_0 values and by using the same ionic strength of sodium sulfate as the diffusion experiment. Since a dynamic equilibrium may exist between C_0 and C_s in the cylindrical film roll method, in which a stagnant layer effect on the surface of the substrate cannot be inevitable, the values of $-\Delta\mu^0$ estimated are approximate ones. But the estimation of $-\Delta\mu^0$ from the C_0 values of the film roll method may be one feasible procedure to obtain the value for active species under alkaline conditions. The approximate coincidence of these values with the values estimated by other workers[31,32] may suggest the validity of this conclusion.

MCT dyes, having 6–12 kJ mol^{-1} as the values of $-\Delta\mu^0$, may be used for all-purpose application, those having values more than 14 kJ mol^{-1} for exhaust dyeing, and those having values of 5–6 kJ mol^{-1} only for printing and continuous dyeing. Thus, by the introduction of MCT groups, the substantivity as well as the reactivity of reactive dyes may be widely altered

TABLE 5
Value of $-\Delta\mu^0$ for Various Reactive Dyes on Cellophane

CI Reactive	*Reactive groups*	*Temp. (°C)*	*pH*	$-\Delta\mu^0$ *kJ mol^{-1}*	*Reference*
Red 120	Monochlorotriazinyl	80	6.8	24.1	This study
(Red E)			6.8	16.8	This study
Yellow 3	Monochlorotriazinyl	80	6.8	11.1	26
Red 3	Monochlorotriazinyl	80	6.8	6.5	26
Blue 2	Monochlorotriazinyl	80	6.8	9.3	26
Yellow 4	Dichlorotriazinyl	30	6.8	15.8	27
Orange 1	Dichlorotriazinyl	30	6.8	12.9	27
Red 1	Dichlorotriazinyl	30	6.8	9.8	27
Blue 4	Dichlorotriazinyl	30	6.8	5.0	28
Yellow 17	Vinylsulfonyl	49	10.5	4.8	29
Orange 7	Vinylsulfonyl	49	10.5	4.2	29
Red 22	Vinylsulfonyl	49	10.5	5.2	29
Blue 19	Vinylsulfonyl	49	10.5	3.8	29
Black 5	Vinylsulfonyl	49	10.5	6.3	29
Red 17	Trichloropyrimidyl	80	10.5	7.0	30
Red 41	2,3-Dichloroquinoxaline-6-carbonyl	50	10.5	5.5	30

at need. Red E has 17 kJ mol^{-1} as the value of $-\Delta\mu^0$, implying that it can be applied as a typical reactive dye for exhaust dyeing.

The values of $-\Delta\mu^0$ for dichlorotriazinyl (DCT) dyes are in the range between 5 and 16 kJ mol^{-1} at 30°C (Table 5). Although the application temperature is different from that for MCT dyes, typical reactive dyes have 5–15 kJ mol^{-1} as values of $-\Delta\mu^0$. These dyes may be used for all-purpose application. This fact can also be confirmed for trichloropyrimidinyl and dichloroquinoxaline carbonyl dyes.[30] Sumner & Taylor[31] determined the values of $-\Delta\mu^0$ for three DCT dyes. The values decreased with increase in the dye concentration. This may be the same phenomenon as observed above in the cases of the determination of the values at low salt concentration.

On the other hand, VS dyes have low values of $-\Delta\mu^0$ in general. They are too small to give high fixation. VS dyes must be applied by the simultaneous adsorption/diffusion/reaction process to obtain deep dyeing.

Compared with the values for exhaustion dyeing, CI Reactive Red 120 has a very large value of $-\Delta\mu^0$, although it is still smaller than that for CI Direct Blue 1. Reactive dyes with too high a substantivity have been considered not to be desirable because the unreacted dye cannot be removed easily by washing off, after the reactive dyeing process, and because such dyes have too low diffusion coefficients. However, the saturation phenomenon of adsorption may solve the latter defect. These problems will be discussed in future papers.

4. SUMMARY

The adsorption of two MCT reactive dyes (CI Reactive Red 120 and a similar red dye with one MCT group (Red E)) on cellulose was investigated over a wide concentration range of sodium sulfate and compared with the adsorption behavior of CI Direct Blue 1. The values of $-\Delta\mu^0$ for CI Reactive Red 120, Red E, and CI Direct Blue 1 were constant at intermediate concentrations of sodium sulfate. At high salt concentrations, the dyes examined showed saturation phenomena of adsorption and a decrease in the value of $-\Delta\mu^0$. At low salt concentrations, all three dyes had apparently higher substantivity to cellulose than that at higher salt concentrations because of the large contribution of impregnation of dye solution.

The values of $-\Delta\mu^0$ for usual reactive dye ranges with various reactive groups were considerably smaller than those for the MCT dyes determined in the present paper, as expected. There may be some possibility to resolve the low fixation problem of reactive dyeing under low electrolyte conditions by reference to the results obtained in this investigation.

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