Developing an Equilibrium Equation for Direct Dye Mixtures on Cellulose

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ABSTRACT

An equilibrium equation has been developed to correlate data for direct dye/cotton systems containing single dyes, mixtures of two dyes, and cotton fibers containing carboxyl groups. The data for Direct blue 1, red 2, red 81 and yellow 12 at 90°C can be explained in terms of a modified Langmuir equation that can account for positive and negative dye interactions on the fiber. Standard chemical potentials are tabulated and sorption isotherms are plotted for the dye systems evaluated.

The textile industry in the U.S. currently processes over 13 billion pounds of fiber annually [10]. While much of the cotton or cellulose is dyed with mixtures of dyes, very little information has been published on the mechanism of dyeing cellulose with direct dye mixtures. The first attempt to investigate the equilibrium of direct dye mixtures on cellulose was made by Neale and Stringfellow [7], but they did not propose an equation to describe the equilibrium. Because essentially all of the equilibrium equations for dyes on cellulose were reported to follow the Freundlich [2] equation, which assumes an unlimited number of sites on the fiber, no quantitative account was proposed for the competition direct dye mixtures have for the surface of the fiber [7]. In this paper, we analyze the experimental data of Neale and Stringfellow [7] and develop equilibrium equations to describe a system containing a single dye, a system containing a mixture of two dyes, and a system containing cotton fiber in various stages of oxidation.

Discussion

Since the dye/fiber system examined in this paper uses direct anionic dyes, the equations used to describe the equilibrium must take into account the sodium ions that are present with the dye anion. Equation 1 shown below is the Freundlich equation [2],

$$K = \frac{(D_f Na_i^z)^x}{D_s Na_s^z} \quad , \tag{1}$$

where the Na term represents the sodium ion concentration at equilibrium in the fiber internal volume Na_i and in the external solution Na_s, respectively. The term z represents the total charge on the dye anion. For this equation, the internal solution is identified as the solution within the fiber [11] that is influenced by the fiber, and it is illustrated in Figure 1. The Langmuir equation [4] can also be used to describe direct dye sorption [9] and is shown below:

$$K = \frac{\dfrac{D_f}{\text{sat.} - D_f} Na_i^z}{D_s Na_s^z} \quad . \tag{2}$$

The Na term, as stated above, represents the sodium ion concentration in the fiber or in the dyebath, and sat. is the saturation value for the fiber.

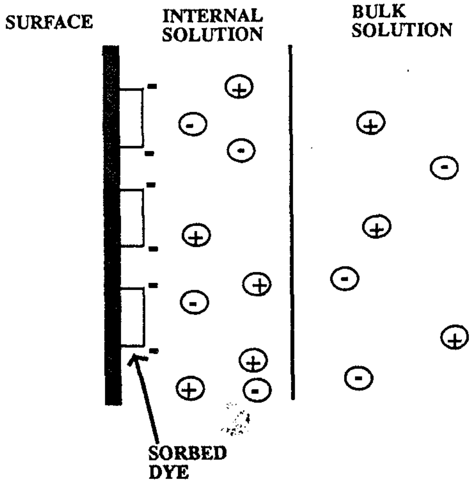

FIGURE 1. Schematic representation of an internal solution.

When no added salt is present in the dyebath, the sodium ion concentration on the fiber is equal to z times the dye concentration on the fiber. When added salt is present in the dyebath, the sodium ion concentration on the fiber will not be equal to z times the dye concentration and therefore must be calculated indirectly. This can be done if two basic assumptions of

Donnan are made [1] and used with the equations shown above. First, the fiber in the dyebath with its internal solution is assumed to be electrically neutral, that is, the total (+) charge is equal to the total (−) charge within the fiber. Second, the standard chemical potential of the internal solution and the external dyebath solution are assumed to be equal [11]. When these two assumptions are made, the following equation can be derived, which allows the sodium ion concentration within the fiber to be calculated:

$$Na_i^+ = \frac{D_f}{V}\left\{\frac{z}{2} + \left(\frac{z^2}{4} + \frac{Na_s\mathrm{Cl}_sV^2}{D_f^2}\right)^{1/2}\right\} \quad . \qquad (3)$$

The subscripts f, s, and i refer to the fiber, the dyebath, and the internal solution, respectively. V represents the volume of the internal pore solution and will vary and depend on the morphology of the fiber substrate. In this case the substrate is cotton cellulose.

We can calculate the standard chemical potential of dyeing [11], commonly referred to as the affinity, in the following equation:

$$-\Delta\mu^0 = RT\ln K \quad , \qquad (4)$$

Standard Chemical Potential

where K represents the equilibrium constant shown in Equations 1 and 2, R is the gas constant in units of calories per degree per mole, and T is the temperature in Kelvins. This has been done for the four dyes illustrated in Figure 2. To make calculations using Equation 2, it was first necessary to estimate a saturation value (sat.) by rearranging Equation 2 into the following form:

$$\frac{1}{D_f} = \frac{1Na_s^z1 \cdot 1}{D_sNa_i^z\text{sat.}K} + \frac{1}{\text{sat.}} \quad . \qquad (5)$$

Langmuir Equation in Reciprocal Form

Using Equation 5, a least squares plot of the data was generated and extrapolated so that an estimation of the sat. value for the dye could be made. The standard chemical potentials were then calculated from Equations 1, 2, and 4 and are shown in the upper part of Tables I-VI. The Freundlich affinities calculated from Equations 1 and 4 agree with those reported by other workers [11].

Using the computer, the value for V previously reported [11] was allowed to vary to see if a better correlation could be obtained with the data with other values of V. No better overall agreement could be obtained in this effort, so all data are reported using the value of V equal to 0.22 l/kg for cotton cellulose.

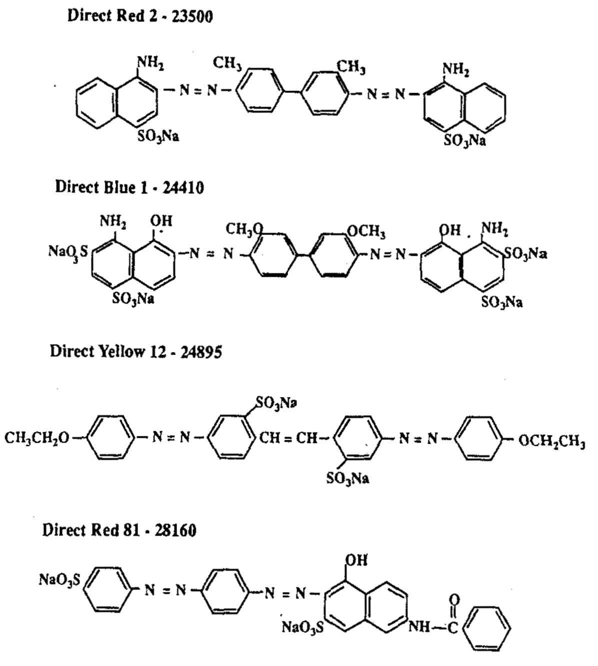

FIGURE 2. Dye structures.

The Langmuir affinities were also calculated using Equations 2 and 4 and the saturation values giving the best correlation of the data. These results are shown in Table I-VI. The affinities calculated with Equation 2 gave a much smaller percent coefficient of variation than those calculated with Equation 1.

MIXTURE DYEINGS

When the dyes shown in Figure 2 are used as mixtures of two dyes in the same dyebath, a striking suppression of the sorption occurs. This is dramatically illustrated in Figure 3, where Direct blue 1 was held at constant dyebath concentration while Direct yellow 12, Direct red 81, and Direct red 2 were added at increasing concentrations and suppressed the sorption of blue 1 with no consistent behavior visible [7]. The sorption of Direct blue 1 on oxidized cellulose is also shown for comparison in Figure 3 [6]. All of the results are plotted as equivalent concentrations to eliminate differences due to the different charges on the dye anions. We attempted to interpret the data in Figure 3 in terms of an affinity equation reported earlier [9] for mixtures of dibasic direct dyes, but this was not successful. In our earlier work [9], all of the dyes we used were dibasic direct dyes and were applied at almost constant ratios over the concentration ranges studied. The dyes presented in this paper are both dibasic and tetrabasic and were applied at varying ratios. For example, in Figure

3 Direct blue 1 is maintained at a constant dyebath concentration, while the second dye in the bath is varied in concentration. This appears to place greater demands on the mathematical analyses than our previous work [9], where the two dye concentrations were applied in a constant ratio.

TABLE I. Calculation of affinity of Direct blue 1 with red 2 in dyebath on cotton fiber at 90°C.[a]

Blue 1		Red 2		Affinity	
On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/kg $(\cdot 10^6)$	On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/kg $(\cdot 10^6)$	Freundlich, Eq. 1	Langmuir, Eq. 2
2.50	10.07			−5826	−7339
3.60	25.18			−5746	−7289
4.73	50.36			−5761	−7337
5.87	100.72			−5715	−7325
7.20	201.45			−5686	−7337.
7.96	302.17			−5634	−7310
Average				−5728	−7323
Range				191	49
% Coef. variation				1.15	0.27
Mixture with red 2 in Table II					Eq. 6
3.12	50.36	5.93	11.04	−5820	−7204
2.32	50.36	10.90	34.50	−6018	−7283
1.54	50.36	15.45	68.99	−6063	−7234
2.79	100.72	12.69	68.99	−5957	−7197
3.88	151.09	11.04	68.99	−5953	−7245
Average				−5962	−7233
Range				243	86
% Coef. variation				1.53	0.48

[a] Charge on dye = 4, internal volume = 0.22 l/kg, coefficients for Equation 6 are $x = 1$ and $y = -1$, sat. value used = 0.0295 mole/kg, NaCl conc. = 0.0855 mole/l, M.W. blue 1 = 993.

TABLE II. Calculation of affinity of Direct red 2 with blue 1 in dyebath on cotton fiber at 90°C.[a]

Red 2		Blue 1		Affinity	
On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/kg $(\cdot 10^6)$	On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/kg $(\cdot 10^6)$	Freundlich, Eq. 1	Langmuir, Eq. 2
9.66	11.04			−6690	−8372
14.76	34.50			−6501	−8381
17.66	68.99			−6298	−8320
21.66	137.98			−6155	−8434
24.15	275.97			−5850	−8353
Average				−6299	−8372
Range				839	115
% Coef. variation				5.11	0.50
Mixture with blue 1 in Table I					Eq. 6
5.93	11.04	3.12	50.36	−6502	−8407
10.90	34.50	2.32	50.36	−6326	−8358
15.45	68.99	1.54	50.36	−6247	−8413
12.69	68.99	2.79	100.72	−6088	−8322
11.04	68.99	3.88	151.09	−6013	−8374
Average				−6235	−8375
Range				490	91
% Coef. variation				3.12	0.44

[a] Charge on dye = 2, internal volume = 0.22 l/kg, coefficients for Equation 6 are $x = 1$ and $y = 3$, sat. value used = 0.031 mole/kg, NaCl conc. = 0.0855 mole/l, M.W. red 2 = 725.

Morita *et al.* [5] have reported work with mixtures of some of the same dyes shown in Figure 2. They interpreted the data in terms of the Freundlich equation, Equation 1, and obtained variations with their calculated affinities similar to those we report here with the same equation. They applied the dyes in constant

TABLE III. Calculation of affinity of Direct blue 1 with red 81 in dyebath on cotton fiber at 90°C.[a]

Blue 1		Red 81		Affinity	
On fiber, mole/kg ($\cdot 10^3$)	In soln., mole/l ($\cdot 10^6$)	On fiber, mole/kg ($\cdot 10^3$)	In soln., mole/l ($\cdot 10^6$)	Freundlich, Eq. 1	Langmuir, Eq. 2
2.50	10.07			−5826	−7339
3.60	25.18			−5746	−7289
4.73	50.36			−5761	−7337
5.87	100.72			−5715	−7325
7.20	201.45			−5686	−7337
7.96	302.17			−5634	−7310
Average				−5728	−7323
Range				191	49
% Coef. variation				1.15	0.27
Mixture with red 81 in Table IV					Eq. 6
3.00	50.36	2.77	74.01	−5333	−7176
2.26	50.36	4.26	148.02	−5124	−7178
1.38	50.36	6.10	296.03	−4774	−7222
0.89	50.36	7.27	444.05	−4473	−7381
3.81	100.72	3.85	148.02	−5359	−7421
5.68	201.45	2.62	148.02	−5456	−7397
7.05	302.17	2.07	148.02	−5569	−7487
Average				−5155	−7323
Range				1097	311
% Coef. variation				7.71	1.75

[a] Charge on dye = 4, internal volume = 0.22 l/kg, coefficients for Equation 6 are $x = 1$ and $y = 3.4$, sat. value used = 0.0295 mole/kg, NaCl conc. = 0.0855 mole/l, M.W. blue 1 = 993.

TABLE IV. Calculation of affinity of Direct red 81 with blue 1 in dyebath on cotton fiber at 90°C.[a]

Red 81		Blue 1		Affinity	
On fiber, mole/kg ($\cdot 10^3$)	In soln., mole/l ($\cdot 10^6$)	On fiber, mole/kg ($\cdot 10^3$)	In soln., mole/l ($\cdot 10^6$)	Freundlich, Eq. 1	Langmuir, Eq. 2
3.92	74.01			−4253	−6692
5.57	148.02			−4126	−6744
Average				−4189	−6718
Range				127	52
% Coef. variation				2.15	0.55
Mixture with blue 1 in Table III					Eq. 6
2.77	74.01	3.00	50.36	−4351	−6824
4.26	148.02	2.26	50.36	−4161	−6758
6.10	296.03	1.38	50.36	−3921	−6709
7.27	444.05	.89	50.36	−3764	−6713
3.85	148.02	3.81	100.72	−4265	−6907[b]
2.62	148.02	5.68	201.45	−4142	−6747
2.07	148.02	7.05	302.17	−4098	−6720
Average				−4100	−6768
Range				586	198
% Coef. variation				4.88	1.08

[a] Charge on dye = 2, internal volume = 0.22 l/kg, coefficients for Equation 6 are $x = 1$ and $y = 0.5$, sat. value used = 0.0114 mole/kg, NaCl conc. = 0.0855 mole/l, M.W. red 2 = 676. [b] When this point is excluded from the data, the CV is reduced to 0.74.

ratios over the sorption range and obtained affinities that varied significantly. It was our objective in this work to derive an equilibrium equation that would better correlate the experimental data. In the following

TABLE V. Calculation of affinity of Direct blue 1 with yellow 12 in dyebath on cotton fiber at 90°C.[a]

Blue 1		Yellow 12		Affinity	
On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/l $(\cdot 10^6)$	On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/l $(\cdot 10^6)$	Freundlich, Eq. 1	Langmuir, Eq. 2
2.50	10.07			−5826	−7339
3.60	25.18			−5746	−7289
4.73	50.36			−5761	−7337
5.87	100.72			−5715	−7325
7.20	201.45			−5686	−7337
7.96	302.17			−5634	−7310
Average				−5728	−7323
Range				191	49
% Coef. variation				1.15	0.27
Mixture with yellow 12 in Table VI					Eq. 6
0.19	10.07	4.35	293.83	−3921	−7378
0.30	25.18	4.33	293.83	−3619	−7108
0.62	50.36	4.23	293.83	−3720	−7253
1.29	50.36	2.79	146.91	−4233	−7037
2.17	50.36	1.91	73.46	−4738	−7283
1.29	100.72	3.67	293.83	−3851	−7162
2.78	201.45	2.89	293.83	−4209	−7375
Average				−4042	−7228
Range				1119	341
% Coef. variation				9.49	1.81

[a] Charge on dye = 4, internal volume = 0.22 l/kg, coefficients for Equation 6 are $x = 0.334$ and $y = 0.169$, sat. value used = 0.0295 mole/kg, NaCl conc. = 0.0855 mole/l, M.W. blue 1 = 993.

TABLE VI. Calculation of affinity of Direct yellow 12 with blue 1 in dyebath on cotton fiber at 90°C.[a]

Yellow 12		Blue 1		Affinity	
On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/l $(\cdot 10^6)$	On fiber, mole/kg $(\cdot 10^3)$	In soln., mole/l $(\cdot 10^6)$	Freundlich, Eq. 1	Langmuir, Eq. 2
2.09	73.46			−3664	−6222
3.00	146.91			−3493	−6163
4.44	293.83			−3381	−6273
Average				−3513	−6219
Range				283	110
% Coef. variation				4.05	0.89
Mixture with blue 1 in Table V					Eq. 6
4.35	293.83	0.19	10.07	−3388	−6285
4.33	293.83	0.30	25.18	−3401	−6306
4.23	293.83	0.62	50.36	−3422	−6345
2.79	146.91	1.29	50.36	−3617	−6366
1.91	73.46	2.17	50.36	−3909	−6607[b]
3.67	293.83	1.29	100.72	−3374	−6267
2.89	293.83	2.78	201.45	−3354	−6269
Average				−3495	−6349
Range				555	339
% Coef. variation				5.79	1.88

[a] Charge on dye = 2, internal volume = 0.22 l/kg, coefficients for Equation 6 are $x = 1$ and $y = 0.6$, sat. value used = 0.00843 mole/kg, NaCl conc. = 0.0855 mole/l, M.W. yellow 12 = 681.

[b] When this point is excluded from the data, the CV is reduced to 0.65.

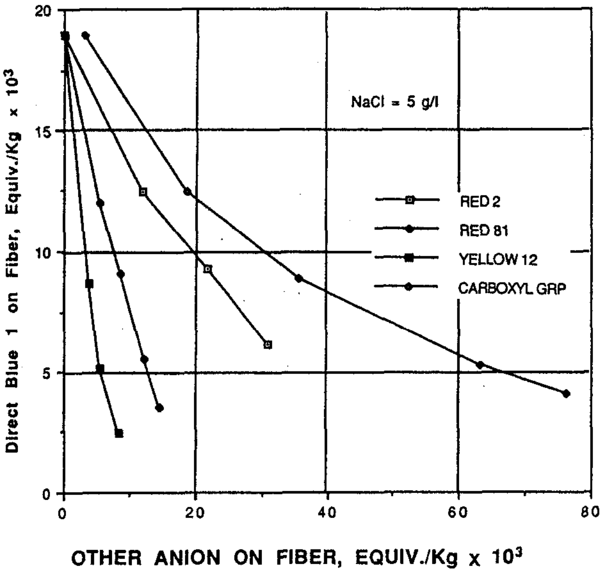

FIGURE 3. Sorption of Direct blue 1 on cotton with one other dye or carboxyl groups on fiber at 90°C.

sections, we discuss the specific factors affecting sorption and evaluate data obtained with the individual dye mixtures.

FACTORS INFLUENCING MIXTURE DYE SORPTION

The factors that could affect the sorption of a direct dye when it is used in the presence of another dye are as follows:

1. Competition of the two dye anions for available sorbing surface.
2. Decrease in sorption of either dye anion in the mixture because of the increase in total concentration of sodium ions on the fiber contributed by both dyes. When Na_1 is calculated from Equation 3 for both dyes on the fiber, and then used in Equation 2 to calculate a D_f on the fiber for the individual dye, the calculated value of D_f will be lower even if no interaction of the dyes occurs on the fiber and no space limitations exist.
3. Electrical repulsion of a dye from the fiber surface by other sorbed dyes of like charge.
4. Attraction of dyes for each other on the fiber surface.
5. Interaction of direct dyes with each other in solution.

The last factor of this list, 5, does not appear to be influencing the sorption of the dyes presented here because of the temperature used. All dyeings were conducted at 90°C, and there was no evidence to support solution interaction [7] at this temperature. This observation was in agreement with the results we reported in our earlier work [9].

We evaluated several simple equilibrium equations to find one that best correlated the data for the mixture dyeings. We attempted to use a mole fraction for the internal solution sodium ion concentration based on the two dye concentrations present on the fiber, but these were unsuccessful. For the dye ions in the dyebath, we obtained the best correlations using the actual dye concentrations present in the bath. After much experimentation, we selected the following equation as giving the best correlation of the experimental data:

$$K = \dfrac{\dfrac{D_{fa} Na_i^z}{\text{sat.}_a - D_{fa} - y D_{fb}^x}}{D_{sa} Na_s^z} \quad , \qquad (6)$$

Modified Langmuir Equation

where the subscripts a and b refer to the two different dyes under study and f, i, and s refer to the fiber, internal solution, and solution, respectively. The coefficients x and y are determined for the secondary dye D_{fb} in the mixture. This equation approaches Equation 2 when the secondary dye concentration approaches zero on the fiber.

Using Equation 6 and a personal computer, we determined values for x and y by trial and error and calculated the affinities. These are presented in the lower part of Tables I-VI. The percent coefficients of variation were generally good and the mixture dyeing affinities agreed remarkably well with the affinities for the single dyeings. The values reported for x, y, and the saturation values were selected as giving the best overall correlation of the data. When the constants were optimized for each individual case, the correlation was only slightly improved for two of the six cases evaluated.

To visually see the correlation and interpret the experimental data, four curves are plotted in each of the Figures 4-7. The curves shown in each figure are described as follows:

Plot 1: A plot of the single dye sorption isotherm. Labeled "alone".

Plot 2: A plot of the sorption isotherm when varying concentrations of a second dye are added to the bath. Labeled "with other dye".

Plot 3: A plot of the calculated concentration of dye "A" that would be obtained if the only factor lowering the sorption of dye "A" were the presence of added sodium ion (common ion) on the fiber attributed to the second dye "B". Equation 2 was used to calculate

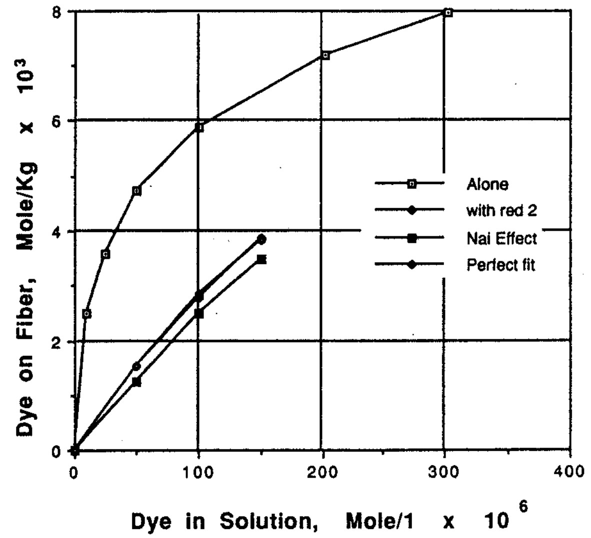

FIGURE 4. Sorption of blue 1 alone and with red 2 on cotton fiber at 90°C.

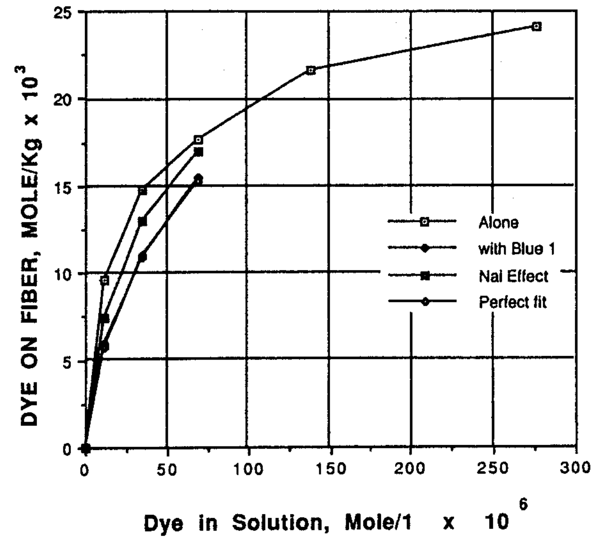

FIGURE 5. Sorption of red 2 alone and with blue 1 on cotton fiber at 90°C.

the concentration of dye "A" when Na_i was contributed by both dyes on the fiber. Labeled "Na_i effect".

Plot 4: A calculated plot that would have been obtained if perfect agreement were achieved with Equation 6. Equation 6 was used to solve for a value of dye "A" that would give perfect agreement when the experimentally determined concentration of the second dye, "B", was present on the fiber. Labeled "perfect fit".

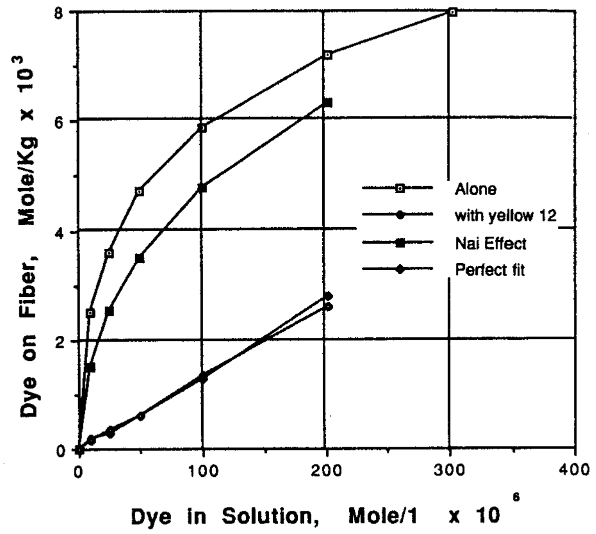

FIGURE 6. Sorption of blue 1 alone and with yellow 12 on cotton fiber at 90°C.

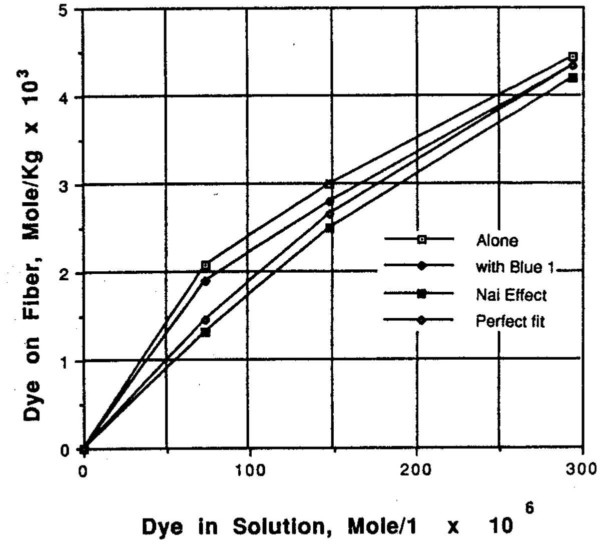

FIGURE 7. Sorption of yellow 12 alone and with blue 1 on cotton fiber at 90°C.

AGREEMENT OF DATA WITH EQUATION 6

The overall agreement was good for the three dye mixtures and very good for blue 1 and red 2 shown in Figures 4 and 5, where the actual data plot and theoretical plot are almost identical. The deviation was greater for yellow 12 shown in Figure 7. However, when one point was eliminated from the calculated average shown in Tables IV and VI, the correlation was very good for both red 81 and yellow 12. Considering the added difficulty in spectrophotometrically measuring two dyes in a solution at varying concentration ratios, the agreement with Equation 6 was satisfactory. The results also indicate that two or three of the factors mentioned above may operate jointly to affect the sorption of a dye when it is used in a mixture.

The affinities calculated by the Freundlich equation (Equation 1) for the mixture dyeings are shown in the lower part of Tables I-VI to illustrate how this equation gives a poorer correlation when it is applied to a system containing two dyes. The modified Langmuir equation (Equation 6) takes into account the presence of a second dye and may be used to give a quantitative measure of the effect each dye has in the mixture. This is illustrated in Table VII, which gives the values for the coefficients x and y and lists the saturation values used for their calculations. We will now examine each mixture in more detail to interpret the results obtained.

Red 2 and Blue 1 Mixture

The data for blue 1 and red 2 shown in Tables I and II and plotted in Figures 4 and 5 illustrate the case where Direct red 2 actually interacts with blue 1 on the fiber so as to increase its sorption over that expected. If no competition for surface or interaction of the dyes occurred on the fiber, a decrease in sorption of each dye would be expected. As discussed earlier, this is due to an increase in the total sodium ion concentration on the fiber contributed by both dyes. If this were the case, the actual curves for the dyes when present in the mixture would be equal to the Na_i effect curve shown in Figures 4 and 5. The Na_i effect curve in Figure 4 is the calculated concentration of blue 1 that would be sorbed in the presence of the measured concentration of red 2 on the fiber. In Figure 4, the actual sorption of blue 1 in the mixture (labeled "with Red 2") is greater than that calculated for the Na_i effect curve. The concept of attractive interaction of red 2 for blue 1 on the fiber is in agreement with the negative coefficient (−1) shown at the bottom of Table I. The similarity of the molecular structures of red 2 and blue 1 shown in Figure 2 would support the possibility of complex formation on the fiber.

In the case of red 2 shown in Figure 5, blue 1 suppresses the sorption of red 2 more than would be calculated by the common ion effect of sodium and shown as the Na_i effect curve. This is illustrated by the positive value of 3 obtained for the coefficient for red 2 in Table II. If Equation 6 is correct, the blue 1 dye appears to block out three molecules of red 2 dye per molecule of blue 1 sorbed. Either physical blocking or electrical repulsion may contribute to this effect, since the available information will not distinguish which is occurring. No doubt in Figure 3 the decrease in sorption of blue 1 caused by the presence of carboxyl groups on cotton fiber [6] can be accounted for by the carboxylate ion rather than surface competition. The location of the carboxyl groups within the fiber, which were produced by a chemical reaction, should be very different from that of the dye molecule on the fiber and give very different results. The direct dye molecules are believed to prefer the ordered areas near the crystal regions [11], while the chemically formed carboxyl group may be near the surface or unordered accessible regions of the fiber.

It is surprising to imagine that red 2 on the fiber attracts blue 1 to the fiber, while at the same time blue 1 blocks red 2 from the fiber. The hydrogen or van der Waals bonding side of the dye molecule would be ex-

TABLE VII. Constants used in Equations 1-6 for affinity calculations for direct dyes on cotton fiber at 90°C.[a]

Dye	Charge on dye	Saturation value moles/kg	Coefficients for Equation 6		% Coef. of variation		
			X	Y	Eq. 1, Fruend.	Eq. 2, Lang.	Eq. 6, mixture
Red 2 & blue 1							
Red 2	2	0.031	1	3	5.11	0.50	0.44
Blue 1	4	0.0295	1	−1	1.15	0.27	0.48
Red 81 & blue 1							
Red 81	2	0.0114	1	0.44	2.15	0.55	1.05[b]
Blue 1	4	0.0295	1	3.4	1.15	0.27	1.75
Yellow 12 & blue 1							
Yellow 12	2	0.00843	1	0.6	4.05	0.89	1.88[b]
Blue 1	4	0.0295	0.334	0.169	1.15	0.27	1.81

[a] NaCl conc. = 0.0855 moles/liter. [b] When one point is excluded from the data these two values are reduced to 0.74 and 0.65, respectively.

pected to face the cellulose surface, while the sulfonate groups face the aqueous internal solution within the fiber [11]. In this case, the four negative charges on the blue 1 dye would be more likely to prevent interaction with an approaching dye molecule than the two charges on the red 2 dye. The results reported here agree with this concept and the specific nature of dye-dye interactions. While interaction is proposed on the fiber we obtained no evidence for the single dye aggregation here or in previous work [9] at 90°.

The saturation value used for blue 1 and red 2 is approximately half of that reported by Neale and Stringfellow [7], but may be explained by the fact that their results were obtained at much higher sodium chloride concentrations. Our previous work has shown that the saturation value can increase with increasing salt concentration [9].

RED 81 AND BLUE 1 MIXTURE

The data for blue 1 and red 81 are represented in Tables III and IV. The figures for these two dyes are not shown to conserve journal space. Both of these dyes decrease the sorption of the other dye more than can be explained by the common ion effect of sodium. Direct red 81 blocks the sorption of blue 1 by a factor of 3 to 4 according to the value of the *y* coefficient obtained from Equation 6 and shown in Table III. When one dye molecule blocks several other dye molecules, as noted earlier with blue 1 and red 2, it is believed to occur by electrical repulsion rather than physical blocking of specific fiber surface. More support for this concept may be obtained by comparing data taken at different salt concentrations. The field repulsion effects should be more sensitive to ionic strength than the physical blocking effects and decrease more rapidly as salt concentration increases. The concentration of salt used in these experiments was 5 g/l, which is not low and should tend to minimize the electrical repulsion of like charged dyes. With this pair of dyes, blocking by either dye decreases at the higher dye concentrations.

The effect that blue 1 has on the sorption of red 81 is small and accounts for the small *y* coefficient of only 0.5, indicating that about one-half of the sorbed blue 1 molecules block the red 81 dye. Evidently the difference in molecular structure and site selection of these two dyes separates them sufficiently on the fiber so that interaction is much less than that observed with blue 1 and red 2. Much of the effect of blue 1 on red 81 may be attributed to the common sodium ion effect rather than specific dye interaction.

YELLOW 12 AND BLUE 1 MIXTURE

The data for blue 1 and yellow 12 are given in Tables V and VI and plotted in Figures 6 and 7. As the curves in Figure 3 illustrate, the effect of yellow 12 on the sorption of blue 1 was the most dramatic of the three dyes. The best agreement for Equation 6 was obtained with a very small value for the *x* coefficient of 0.334 and a value of 0.166 for the *y* coefficient. In this case, the correlation requires the use of an exponential function. Even though the yellow dye has a different structure from that of blue 1, it must be located on the fiber in a very critical position to so effectively displace the blue dye. This is more understandable as an electrical field effect than a surface blocking effect, since it is hard to imagine that yellow 12 can block six to ten molecules of blue 1 by occupying surface area. This case emphasizes the importance of electrical effects when the two dyes try to occupy the same surface. It is possible that yellow 12 has a high affinity for a small number of sites, as the data in Table VI support this concept. As stated earlier, the salt concentration used here was 5 g/l, which would be expected to reduce ionic interactions. More data at different salt concentrations would help to confirm this point and should give a better insight into the charge interactions occurring within the fiber.

The data for yellow 12 with blue 1 in Table VI gave the poorest correlation of the dibasic dyes, as the coefficients of variation in Table VII show. When we omitted one data point taken at the lowest yellow 12 concentration in Table VI from the calculations, the correlation was very good (0.65). One interpretation that may be given for the high affinity obtained at this point is that yellow 12 has a high affinity for a small fraction of the fiber surface available for sorption. This was noted above and should be supported with additional data to confirm the concept. The primary effect that blue 1 has on the sorption of yellow 12 is to lower the sorption by the Na_i effect or common ion effect. This is similar to the explanation given for blue 1 and red 81 above and in agreement with the closeness of the mixture dyeing curve with the Na_i effect curve shown in Figure 7.

BLUE 1 WITH OXIDIZED COTTON

We made one interesting observation when we calculated the affinities of blue 1 for cotton fiber containing various concentrations of carboxyl groups, shown in Table VIII. The results came from a fiber containing carboxylate anions that are chemically fixed to the fiber rather than dye anions that are free to move in the

TABLE VIII. Calculation of affinity of Direct blue 1 on cotton fiber containing carboxyl groups at 90°C.

Blue 1			Total carboxyl groups [6]		Affinity	
On fiber, mole/kg ($\cdot 10^3$)	In soln., mole/kg ($\cdot 10^6$)	pH Soln.	On fiber, mole/kg ($\cdot 10^3$)	As CO_2-ion, mole/kg ($\cdot 10^3$)	Freundlich, Eq. 1	Langmuir, Eq. 2
2.50	10.07	7.00	3.00	0.00[b]	−5826	−7339
3.60	25.18	7.00	3.00	0.00[b]	−5746	−7289
4.73	50.36	7.00	3.00	0.00[b]	−5761	−7337
5.87	100.72	7.00	3.00	0.00[b]	−5715	−7325
7.20	201.45	7.00	3.00	0.00[b]	−5686	−7337
7.96	302.17	7.00	3.00	0.00[b]	−5634	−7310
Average					−5728	−7323
Range					191	49
% Coef. variation					1.15	0.27
With cotton containing higher carboxyl group concentrations [6]						Eq. 6
4.73	50.36	6.20	3.00	0.00[b]	−5761	−7337
3.15	50.36	6.20	19.00	10.37	−5739	−7270
2.26	50.36	6.20	36.00	18.71	−5800	−7306
1.27	50.36	6.20	63.00	30.30	−5833	−7314
1.05	50.36	6.20	76.00	35.14	−5910	−7385
Average					−5809	−7322
Range					171	116
% Coef. variation					1.16	0.58

[a] Charge on dye = 4, internal volume = 0.22 l/kg, coefficients for Equation 6 are $x = 1$ and $y = 0$, sat. value used = 0.0295 mole/kg, NaCl conc. = 0.0855 mole/l, M.W. blue 1 = 993. Ka COOH groups = $0.135 \cdot 10^{-5}$. [b] The best agreement was obtained by excluding these groups, which are believed to exist mostly as esters in the reference fiber [8].

equilibrium. The dye anions are expected to compete for similar areas in the fiber even if they are sorbed on different sites. The carboxylate ions formed from a chemical reaction would be expected to be in the accessible areas of the fiber, possibly near the surface. As the oxidizing agent enters the fiber at the surface, it is expected to react with available glucose units without seeking specific sites as the dye does. If this is true, the carboxyl groups should block very few of the dye anions from their specific sites and only serve to participate in the Donnan equilibrium, which should lower blue 1 sorption.

The results presented in Table VIII agreed very well with this hypothesis, with the exception of the reference sample reported [6] to contain 3 milliequivalents of carboxyl group per kilogram of cotton. All efforts to use these data in the calculations gave poorer correlations. Examination of the literature [8] indicates that most of the carboxyl groups originating in cotton fiber can be attributed to pectins and other polybasic acids. The polybasic acids are easy to remove, but the pectic acid (polygalacturonic acid) is reported to be to a large extent esterified and only hydrolyzed to the carboxylic acid by boiling with 1% sodium hydroxide for 30 minutes [8]. In this case, we believe that a major portion of the carboxyl groups in the reference cotton fiber were not participating in the Donnan equilibrium and were therefore not included in the calculations. The results shown in Table VIII agree with this and correlate very well with Equations 2 and 6 when $y = 0$. The ionization constant used for the carboxyl groups in cotton fiber was 0.135×10^{-5}, less than one tenth of the value of the ionization constant for acetic acid. This is a value that would be expected for carboxylic acids in aqueous alcoholic solvents [4], which are similar to the oxidized cotton used for the data in Table VIII.

It is evident that the data correlate better with the Langmuir equation than the Freundlich equation, which is commonly used. However, the fair correlation of the data with the Freundlich equation offers evidence that the carboxyl groups do not interfere with the dye sites for blue 1 but only participate in the Donnan equilibrium. When only one dye is present in the system or a small fraction of the dye sites are used, both the Freundlich and Langmuir equations will give good correlations of the data. The Langmuir equation is preferred because it can take into consideration the limitation of surface and the presence of other dyes.

Conclusions

The computer makes it possible to evaluate several equilibrium equations that can be applied to direct dye mixtures. In this study, we report the best correlation obtained to date and discuss the development of a modified Langmuir equation, Equation 6, which we use to interpret the sorption of three direct dye mixtures. The calculated affinities were similar to those obtained with the same dyes applied individually. The equation was able to illustrate both attractive dye interaction on the fiber in the case of red 2 with blue 1 and dye repulsion in the case of red 81 or yellow 12 with blue 1. The coefficients of variation were good for three of the six data sets evaluated and very good for four data sets when two data points were omitted. Equation 6, developed for mixture dye sorption, supports the concept that fiber surface competition, total sodium ion concentration on the fiber, and dye interaction on the fiber all occur with direct dye mixtures. While direct dyes select specific locations for sorption on cellulose that may be mutually identical or significantly separated, their sorption in a mixture can be described by a single equilibrium equation. This equation can be useful for quantitatively measuring the effects the dyes have on each other and is consistent with Equation 2 used for a system containing a single dye.

In the case where cellulose contains chemically bound ions such as carboxyl groups, the Langmuir equation can be used to correlate data for direct dye sorption when the carboxyl groups are taken into consideration. This case provides an excellent example of the common ion effect produced by the total sodium ion concentration on the fiber. It would be applicable to systems containing mixtures of direct dyes that add to the total sodium concentration on the fiber but do not interact with each other or compete for surface area.

More work at equilibrium conditions is needed to provide a better evaluation of the quantative effect salt has on the electrical interaction of direct dyes within the fiber. We will also extend this work to other direct dye mixtures on cellulose to evaluate the use of Equation 6 and, we hope, provide better insight into dyeing systems containing mixtures of direct dyes.

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