# *Studies in the Equilibrium Dyeing of Cotton with Direct Dyes: The Determination of the Activity and Affinity of Direct Dyes for Cellulose*

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The three main theories which have been put forth to explain the effect of dye and salt concentration and temperature on the equilibrium dyeing of cellulosic fibres with direct dyes are those suggested by Hanson, Neale and Stringfellow,1) by Willis, Warwicker, Standing and Urquhart,2) and by Peters and Vickerstaff.3) Peters and Vickerstaff are of the opinion that the driving force during dyeing can be best represented by the Gibbs free energy changes involved; they obtained a quantitative measure of the tendency of dye to pass from the aqueous phase to the fibre phase, which they termed as "affinity." These workers in the development of the treatment were faced with the great difficulty of expressing the activity of dye in the fibre phase, as no precise information was available regarding the saturation values of cellulose with regard to direct dyes. They were, therefore, compelled to introduce a term for the volume of cellulosic fibres, the values of which were deduced arbitrarily from the results of the adsorption of Chrysophenine G by cellulosic fibres, which gave linear plots of unit slope when the logarithm of ionic products in fibre and in the solution at equilibrium were plotted. Recently, Daruwalla and D'Silva4) developed a new thermodynamic approach in which the activity of dye in cellulosic fibre substances is expressed in terms of the fraction of total sites occupied at a particular stage of dyeing. On the basis of this thermodynamic approach, they obtained consistent values of affinity for three direct dyes under different experimental conditions.

The present work was undertaken with a view of seeing whether the thermodynamic treatment of Daruwalla and D'Silva could be applied to other direct dyes, dyes with different chemical structures and aggregation tendencies. Attempts have also been made to test the validity of this treatment in explaining the behaviour of Chlorazol Sky Blue FF and Chrysophenine G during dyeing from a mixed dyebath.

## Experimental Procedure

**Materials.**—The cellulosic fibre substance used was $20^s$ yarn made from Indian cotton and from which, by suitable treatments, impurities other than cellulose in the fibre substance were removed. Pure samples of Congo Red (C. I. Direct Red 28), Benzopurpurine 4B (C. I. Direct Red 2), Benzopurpurine 10B (C. I. Direct Red 7), Chloramine Purple 10BC (C. I. Direct Red 61), Chlorazol Corinth GW (C. I. Direct Red 10), Benzocorinth B (C. I. Direct Violet 21), Diazol Violet R (C. I. Direct Violet 43), Chlorazol Blue B (C. I. Direct Blue 6), Chlorazol Blue G (C. I. Direct Blue 10), Durazol Blue 2R (C. I. Direct Blue 71) and Chlorazol Orange RN (C. I. Direct Orange 8) were obtained from commercial dyes by purification, using the technique recommended by Robinson and Mills,5) the purity of the samples was determined from an analysis of the elements present. All the other chemicals used were of Analar quality.

**The Determination of the Heat of Dyeing.**—The determination of the heat of dyeing was carried out by a technique similar to that described by Gilbert,6) in which a fibre containing a constant amount of a dye is brought to equilibrium at different temperatures with solutions containing different amounts of dye. The details of the determination are the same as those mentioned by Daruwalla and D'Silva.4)

**The Determination of the Fibre Degradation of NaOCl-treated Dyed Cotton.**—A definite weight of dyed or undyed cotton was treated with a 50 ml. sodium hypochlorite solution (3 g./l. available chlorine) buffered to pH 7 at 30°C for 3 min. The oxidised sample was washed thoroughly, antichlored, washed, and dried; the fluidity of the solution containing oxidised sample dissolved in a cuprammonium hydroxide solution was then determined according to A. S. T. M. Standards specifications.7)

For the determination of the values of $[D_\phi]$, the amount of dye in the fibre phase (g. ions/kg.) and $[D_\sigma]$, the amount of dye in the solution (g. ions/l.) in equilibrium at different temperatures, the desorption technique for attaining equilibrium was used. This method of approach for obtaining the values of $[D_\phi]$ and the corresponding values of $[D_\sigma]$ at different temperatures was preferred to the

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1) J. Hanson, S. M. Neale and W. A. Stringfellow, *Trans. Faraday Soc.*, **31**, 1718 (1935).

2) H. F. Willis, J. O. Warwicker, H. A. Standing and A. R. Urquhart, ibid., **41**, 506 (1945).

3) R. H. Peters and T. Vickerstaff, *Proc. Roy. Soc.*, **A192**, 292 (1948).

4) E. H. Daruwalla and A. P. D'Silva, *Textile Research J.*, **33**, 40 (1963).

5) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc.*, **A131**, 576 (1931).

6) G. A. Gilbert, ibid., **A183**, 167 (1944).

7) Apparent Fluidity of Dispersions of Cellulose Fibres, D-539-53, A. S. T. M. Standards, Part 10, 233 (1958).

normal method of obtaining these values from adsorption experiments because, in the latter case, longer times are required for the establishment of equilibrium, with a risk of the decomposition of dyes and changes in the structure of the cellulosic fibres. It was found that the affinity values calculated from the appropriate values of $[D_\phi]$ and $[D_s]$ obtained from desorption experiments were close to those recorded in the literature where the adsorption technique for attaining equilibrium conditions between the dye in the fibre substance and the dye in the bath was employed.

## Results and Discussion

For the direct dyes studied, the results of the present investigation indicate that, except for the initial low concentration of adsorbed dye, the values of the heat of dyeing remain constant over a fairly wide range of dye concentration in the fibre, and that, beyond a critical dye concentration, the values tend to decrease continuously as the amount of adsorbed dye in the fibre is increased (Figs. 1–3). The critical dye concentration beyond which the values decrease is peculiar to each dye studied (Table I). In view of the fact that the cellulose-water system is not homogeneous, the sorption affinity of dye will not be identical over all the surface with which dye may come in contact, with the result that the values of the heat of dyeing associated with different portions of cotton will be different. The values of the heat of dyeing generally indicate overall changes in the heat content of the system, but to some extent these values may also be considered to indicate the energy of the association of a particular dye with cellulose. The fact that constant values of the heat of dyeing over a sufficiently wide range of adsorbed dye are obtained in the present study goes to show that, within this range, the dye

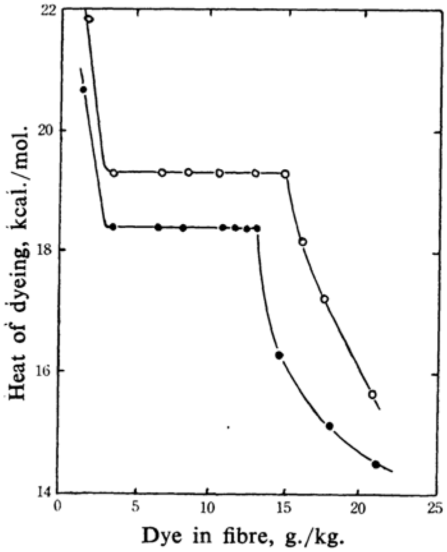


Fig. 1. Heats of dyeing of Benzopurpurine 10B and Benzopurpurine 4B on cotton.

—○— Benzopurpurine 10B
—●— Benzopurpurine 4B

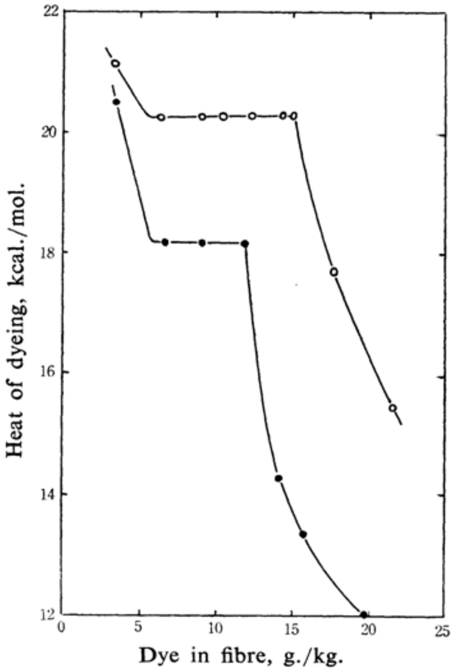


Fig. 2. Heats of dyeing of Chloramine Purple 10BC and Chlorazol Orange RN on cotton.

—○— Chloramine Purple 10BC
—●— Chlorazol Orange RN

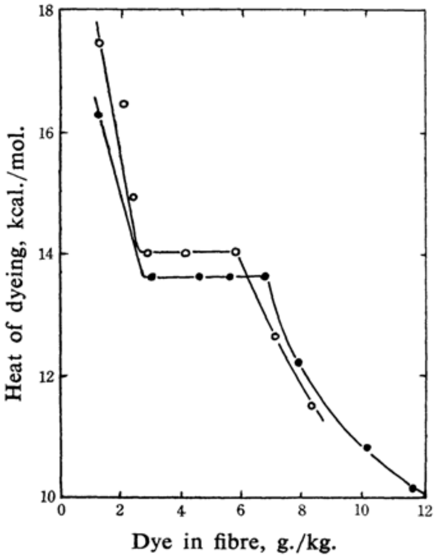
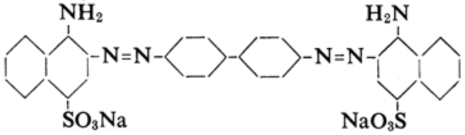
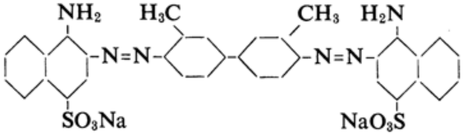
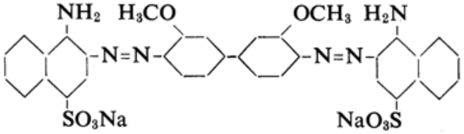
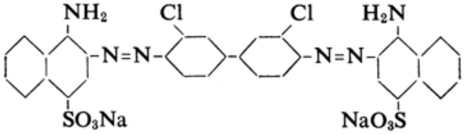
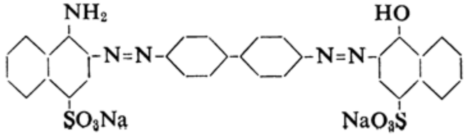
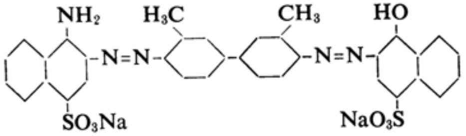
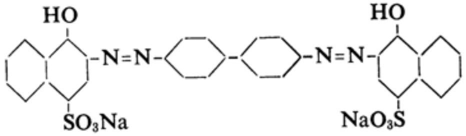
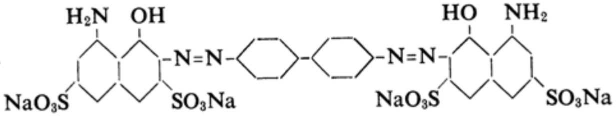
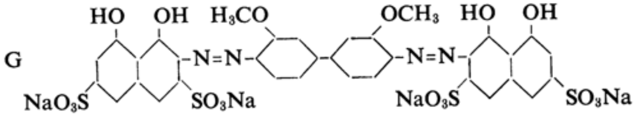
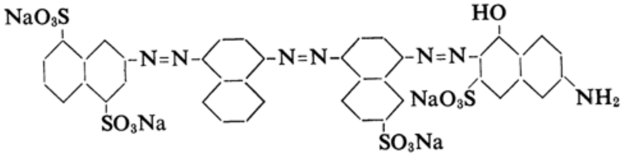
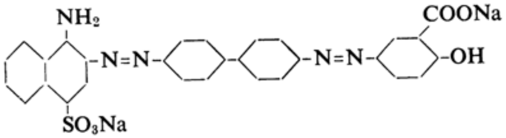


Fig. 3. Heats of dyeing of Chlorazol Blue G and Chlorazol Blue B on cotton.

—○— Chlorazol Blue G
—●— Chlorazol Blue B

TABLE I. HEATS OF DYEING, SATURATION VALUES, AVERAGE AFFINITY VALUES AT DIFFERENT TEMPERATURES AND ENTROPY OF DYEING OF DIRECT DYES ON COTTON

| No. | Dye | Structure | $-\Delta H^\circ$ kcal./mol. (from desorption measurements) | Saturation value mM/kg. dry fibre | | $-\Delta G^\circ$, kcal./mol. | | | | $-\Delta H^\circ$ kcal./mol. (from affinity values) | $\Delta S^\circ$ cal./°C/mol. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 60°C | 70°C | 80°C | 90°C | | |
| 1 | Congo Red |  | 20.24 | 18.67 | B | 9.73 | 9.44 | 9.13 | 8.85 | 19 | 31 |
| | | | | | C | 7.22 | 6.85 | 6.47 | 6.11 | 20 | 39 |
| 2 | Benzopurpurine 4B |  | 18.40 | 17.96 | B | 9.55 | 9.28 | 9.05 | 8.79 | 18 | 27 |
| | | | | | C | 7.32 | 6.98 | 6.69 | 6.36 | 18 | 33 |
| 3 | Benzopurpurine 10B |  | 19.32 | 19.85 | B | 9.28 | 8.97 | 8.74 | 8.40 | 19 | 30 |
| | | | | | C | 7.16 | 6.78 | 6.49 | 6.09 | 19 | 37 |
| 4 | Chloramine Purple 10BC |  | 20.24 | 19.61 | B | 9.98 | 9.71 | 9.44 | 9.17 | 19 | 31 |
| | | | | | C | 7.85 | 7.52 | 7.18 | 6.84 | 19 | 37 |
| 5 | Chlorazol Corinth GW |  | 16.10 | — | C | 7.18 | 6.92 | 6.66 | 6.40 | 16 | 27 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | Benzocorinth B |  | 16.10 | — | C | 7.10 | 6.81 | 6.55 | 6.28 | 16 | 27 |
| 7 | Diazol Violet R |  | 6.0 | — | C | — | — | — | 7.80 | — | — |
| 8 | Chlorazol Blue B |  | 14.03 | 7.24 | B | 7.96 | 7.79 | 7.60 | 7.44 | 14 | 18 |
| | | | | | C | 5.01 | 4.75 | 4.47 | 4.22 | 14 | 27 |
| 9 | Chlorazol Blue G |  | 14.03 | 5.78 | B | 8.14 | 7.96 | 7.79 | 7.61 | 14 | 18 |
| | | | | | C | 4.89 | 4.61 | 4.35 | 4.07 | 14 | 27 |
| 10 | Durazol Blue 2R |  | 21.62 | — | C | 6.85 | 6.40 | 5.95 | 5.50 | 22 | 44 |
| 11 | Chlorazol Orange RN |  | 18.17 | 19.64 | B | 8.56 | 8.34 | 8.11 | 7.90 | 17 | 29 |
| | | | | | C | 6.39 | 6.10 | 5.81 | 5.54 | 17 | 35 |

Mechanism B: Dye anions adsorbed on specific sites and sodium ions diffusely adsorbed.
Mechanism C: Dye anions and sodium ions diffusely adsorbed,

is likely to form a monomolecular layer in the substrate. With further absorption of dye, multimolecular layers are likely to be formed; moreover, because the energy released in sorbate-sorbate interaction is generally lower than that released in the sorbate-solvent interaction, the values of the heat of dyeing show a tendency to decrease as soon as multimolecular layer formation commences. The critical concentration beyond which the values of the heat of dyeing tend to decrease may, therefore, be taken as a stage of the completion of the formation of a monolayer of a particular dye in a cellulosic fibre substance. Although it is not possible to indicate very conclusively whether or not, up to the stage of constancy in the values of the heat of dyeing, a monomolecular layer of the dye is formed in the substrate, indirect evidence in support of this concept is available from the results of the density measurements of dyed cellulose4) and from the results of the oxidation of cellulose containing different amounts of dye with a sodium hypochlorite solution. As did Daruwalla and D'Silva, the present authors found that, in the case of cotton containing increasing amounts of dye (Chloramine Purple 10BC, Chlorazol Orange RN and Chlorazol Blue B), catalytic oxidation is very rapid, but that beyond a critical dye concentration in the fibre, the extent of oxidation does not change appreciably (Fig. 4). This critical dye concentration is analogous to the stage beyond which the values of the heat of dyeing tend to decrease. Thus, because of the formation of a monolayer of dye in cellulose, the dye which is in close proximity to cellulose is more effective in increasing cellulose oxidation than when additional dye going into the fibre gets adsorbed on the monolayer of the dye present in the substrate. Furthermore, as will be discussed later, when these critical concentrations of dyes are considered to be saturation values and when the activity of dye in the fibre and the subsequent affinity values are calculated on the basis of a mechanism of the adsorption of dye anions on specific sites, plots correlating the activity of dye in the fibre with that in solution at equilibrium are linear with slopes close to unity and affinity values are fairly consistent over a wide range of dye concentration in the bath at different dyebath temperatures. Direct evidence is also available from the results of the present study regarding the saturation value of a direct dye for cotton when the reciprocals of the dye in the fibre to that in solution are plotted at different temperatures of dyeing (Fig. 5). These curves are linear, indicating a Langmuir type of adsorption, and the intercept on the $1/[D_\phi]$ axis corresponds to a figure very close to that obtained for monolayer formation from the experiments of the heat of dyeing measurements (Table II).

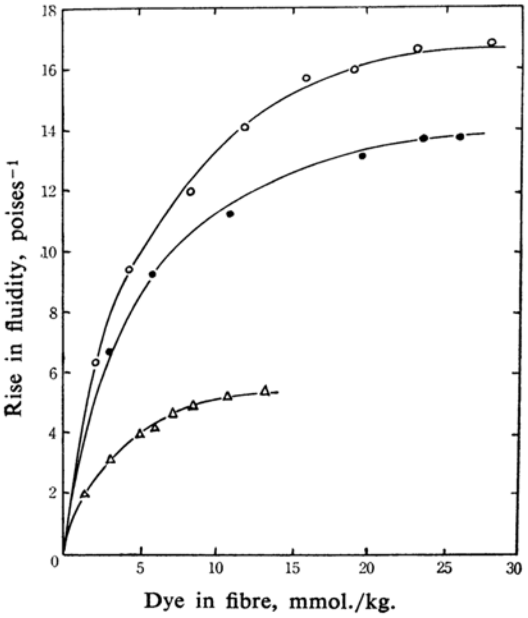


Fig. 4. Relation between rise in fluidity of cotton after oxidation and amount of dye in cotton.

—○— Chloramine Purple 10BC
—●— Chlorazol Orange RN
—△— Chlorazol Blue B

TABLE II. COMPARISON BETWEEN THE SATURATION VALUES OBTAINED FROM HEATS-OF-DYEING MEASUREMENTS AND THOSE OBTAINED FROM ADSORPTION MEASUREMENTS

| Dye | Saturation values obtained from heats of dyeing, mmol./kg. dry fibre | Saturation values obtained from adsorption, mmol./kg. dry fibre |
|---|---|---|
| Congo Red | 18.67 | 17.86 |
| Benzopurpurine 4B | 17.96 | 20.83 |
| Chloramine Purple 10BC | 19.61 | 18.52 |
| Chlorazol Blue B | 7.24 | 8.30 |
| Chlorazol Blue G | 5.78 | 6.17 |

The amounts of dye required for the formation of a monolayer as obtained from the heat of dyeing measurements vary between 6 and 19 mol./kg. of cotton for the different dyes studied. When a comparison is made between the saturation values of different dyes studied, it appears that there is not much difference between dyes of similar structure (namely dye nos. 1–4), but when large sulphonic acid groups are introduced in the dye molecule, as

TABLE III. SLOPES OF PLOTS OF LOG ACTIVITY OF DYE IN FIBRE AND IN DYEBATH

| Dye | Temp. °C | Mechanism A | Mechanism B | Mechanism C |
|---|---|---|---|---|
| Congo Red | 60 | 2.66 | 1.20 | 0.69 |
| | 70 | 2.73 | 1.20 | 0.69 |
| | 80 | 2.70 | 1.18 | 0.70 |
| | 90 | 2.78 | 1.21 | 0.70 |
| Benzopurpurine 4B | 60 | 2.66 | 1.16 | 0.94 |
| | 70 | 2.66 | 1.11 | 0.86 |
| | 80 | 2.56 | 1.08 | 0.84 |
| | 90 | 2.71 | 1.10 | 0.89 |
| Benzopurpurine 10B | 60 | 1.89 | 0.91 | 0.71 |
| | 70 | 1.88 | 0.91 | 0.70 |
| | 80 | 1.80 | 0.91 | 0.67 |
| | 90 | 1.73 | 0.93 | 0.70 |
| Chloramine Purple 10BC | 60 | 2.83 | 1.23 | 0.95 |
| | 70 | 2.63 | 1.16 | 0.90 |
| | 80 | 2.58 | 1.17 | 0.89 |
| | 90 | 2.50 | 1.13 | 0.86 |
| Chlorazol Blue B | 60 | — | 1.60 | 1.20 |
| | 70 | — | 1.53 | 1.20 |
| | 80 | — | 1.58 | 1.21 |
| | 90 | — | 1.55 | 1.20 |
| Chlorazol Blue G | 60 | — | 1.58 | 1.03 |
| | 70 | — | 1.50 | 1.03 |
| | 80 | — | 1.43 | 0.96 |
| | 90 | — | 1.37 | 1.07 |
| Chlorazol Orange RN | 60 | — | 2.28 | 1.78 |
| | 70 | — | 2.22 | 1.67 |
| | 80 | — | 2.06 | 1.50 |
| | 90 | — | 1.91 | 1.45 |

Mechanism A: Dye anions and sodium ions adsorbed on specific sites.
Mechaaism B: Dye anions absorbed on specific sites and sodium ions diffusely adsorbed.
Mechanism C: Dye anions and sodium ions diffusely adsorbed.

in the case of Chlorazol Blue B and Chlorazol Blue G, the saturation values drop appreciably (Table I).

With most of the dyes studied, at a low dye concentration the values of the heat of dyeing are always higher than the normal values, indicating that there exist a limited number of sites in cotton for which dye has high affinity and that, when dye is adsorbed on these highly-active sites, dyeing on the less active and more plentiful sites takes place. These observations are in agreement with those of Gnehm and Kaufler,8) and Jackson and Turner,9) who found that the last traces of direct cotton dyes could not be removed by repeated washing or by extraction with an aqueous solution of pyridine, and with those of Mann and Marrinan,10) who observed that, during the rehydrogenation of deuterated groups in cellulose, a few of these groups were very resistant to rehydrogenation. Very recently, Daruwalla and Shet,11) who studied the kinetics of the rate of the removal of primary adsorbed water in different cellulosic fibres, observed that the rate of removal during the last stages was extremely low compared with the rate of the removal of primary adsorbed water. No correlation was observed between the nitrogen content of the fibre substance or free-COOH groups in the fibre and the amount of dye in the fibre substance where high values of the heat of dyeing are obtained. It appears that the high energy of association between

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8) Von R. Gnehm and F. Kaufler, vide T. Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyd, London (1954), p. 233.

9) J. H. E. Jackson and H. A. Turner, *J. Soc. Dyers Colourists*, **68**, 345 (1952).

10) J. Mann and H. J. Marrinan, *Trans. Faraday Soc.*, **52**, 481 (1956).

11) E. H. Daruwalla and R. T. Shet, *J. Polymer Sci.*, **A2**, 943 (1964).

TABLE IV. ABSORPTION OF BENZOPURPURINE 4B ON COTTON (5 g./l. NaCl)

| Temp. °C | $[D_\phi]$ $10^{-3}$ | $[Na_\phi]$ $10^{-3}$ | $[D_\sigma]$ $10^{-3}$ | $[Na_\sigma]$ $10^{-3}$ | $\theta$ | $-\Delta G^\circ$, kcal./mol. | |
|---|---|---|---|---|---|---|---|
| | | | | | | Mechanism B | Mechanism C |
| 70 | 4.37 | 30.38 | 0.0006 | 85.47 | 0.243 | 9.15 | 7.05 |
| | 5.50 | 31.72 | 0.0009 | 85.47 | 0.306 | 9.17 | 7.00 |
| | 6.17 | 32.54 | 0.0011 | 85.47 | 0.344 | 9.19 | 6.99 |
| | 6.92 | 33.47 | 0.0014 | 85.47 | 0.385 | 9.21 | 6.97 |
| | 7.77 | 34.55 | 0.0017 | 85.47 | 0.433 | 9.26 | 6.96 |
| | 8.72 | 35.80 | 0.0020 | 85.47 | 0.485 | 9.33 | 6.96 |
| 80 | 4.37 | 30.38 | 0.0013 | 85.47 | 0.243 | 8.92 | 6.76 |
| | 6.17 | 32.54 | 0.0023 | 85.47 | 0.344 | 8.95 | 6.69 |
| | 6.92 | 33.47 | 0.0028 | 85.47 | 0.385 | 8.99 | 6.68 |
| | 7.77 | 34.55 | 0.0034 | 85.47 | 0.433 | 9.03 | 6.67 |
| | 8.71 | 35.80 | 0.0041 | 85.47 | 0.485 | 9.10 | 6.67 |
| | 9.78 | 37.22 | 0.0050 | 85.48 | 0.545 | 9.18 | 6.66 |
| 90 | 4.37 | 30.38 | 0.0028 | 85.47 | 0.243 | 8.63 | 6.41 |
| | 6.17 | 32.54 | 0.0048 | 85.47 | 0.344 | 8.68 | 6.35 |
| | 6.92 | 33.47 | 0.0058 | 85.48 | 0.385 | 8.72 | 6.35 |
| | 7.77 | 34.55 | 0.0069 | 85.48 | 0.433 | 8.78 | 6.34 |
| | 8.72 | 35.80 | 0.0083 | 85.48 | 0.485 | 8.84 | 6.34 |
| | 9.78 | 37.22 | 0.0101 | 85.49 | 0.545 | 8.93 | 6.34 |

Mechanism B: Dye anions adsorbed on specific sites and sodium ions diffusely adsorbed.
Mechanism C: Dye anions and sodium ions diffusely adsorbed.

TABLE V. ADSORPTION OF BENZOPURPURINE 10B ON COTTON (5 g./l. NaCl)

| Temp. °C | $[D_\phi]$ $10^{-3}$ | $[Na_\phi]$ $10^{-3}$ | $[D_\sigma]$ $10^{-3}$ | $[Na_\sigma]$ $10^{-3}$ | $\theta$ | $-\Delta G^\circ$, kcal./mol. | |
|---|---|---|---|---|---|---|---|
| | | | | | | Mechanism B | Mechanism C |
| 60 | 5.27 | 31.44 | 0.0004 | 85.47 | 0.265 | 9.30 | 7.31 |
| | 5.91 | 32.31 | 0.0005 | 85.47 | 0.298 | 9.27 | 7.24 |
| | 6.63 | 33.11 | 0.0007 | 85.47 | 0.334 | 9.25 | 7.19 |
| | 7.44 | 34.14 | 0.0009 | 85.47 | 0.375 | 9.22 | 7.12 |
| | 8.35 | 35.30 | 0.0012 | 85.47 | 0.421 | 9.23 | 7.08 |
| | 10.51 | 38.21 | 0.0020 | 85.47 | 0.529 | 9.28 | 7.03 |
| 70 | 5.27 | 31.44 | 0.0009 | 85.47 | 0.265 | 9.01 | 6.96 |
| | 5.91 | 32.21 | 0.0012 | 85.47 | 0.298 | 8.97 | 6.88 |
| | 6.63 | 33.11 | 0.0016 | 85.47 | 0.334 | 8.93 | 6.81 |
| | 8.35 | 35.30 | 0.0027 | 85.47 | 0.421 | 8.93 | 6.71 |
| | 9.36 | 36.68 | 0.0036 | 85.47 | 0.472 | 8.93 | 6.65 |
| | 10.51 | 38.21 | 0.0047 | 85.47 | 0.529 | 8.96 | 6.60 |
| 80 | 5.27 | 31.44 | 0.0019 | 85.47 | 0.265 | 8.79 | 6.68 |
| | 5.91 | 32.21 | 0.0025 | 85.47 | 0.298 | 8.75 | 6.61 |
| | 6.63 | 33.11 | 0.0032 | 85.47 | 0.334 | 8.71 | 6.53 |
| | 8.35 | 35.30 | 0.0055 | 85.48 | 0.421 | 8.69 | 6.41 |
| | 10.51 | 38.21 | 0.0098 | 85.48 | 0.529 | 8.70 | 6.28 |
| | 11.26 | 39.26 | 0.0115 | 85.49 | 0.567 | 8.73 | 6.25 |
| 90 | 5.27 | 31.44 | 0.0043 | 85.47 | 0.265 | 8.45 | 6.27 |
| | 6.63 | 33.11 | 0.0073 | 85.48 | 0.334 | 8.38 | 6.13 |
| | 7.44 | 34.14 | 0.0096 | 85.48 | 0.375 | 8.35 | 6.06 |
| | 9.36 | 36.68 | 0.0163 | 85.50 | 0.472 | 8.36 | 5.95 |
| | 10.51 | 38.21 | 0.0210 | 85.51 | 0.529 | 8.40 | 5.91 |
| | 11.26 | 39.26 | 0.0252 | 85.52 | 0.567 | 8.42 | 5.86 |

Mechanism B: Dye anions adsorbed on specific sites and sodium ions diffusely adsorbed.
Mechanism C: Dye anions and sodium ions diffusely adsorbed.

TABLE VI. ADSORPTION OF CHLORAMINE PURPLE 10BC ON COTTON (5 g./l. NaCl)

| Temp. °C | $[D_\phi]$ $10^{-3}$ | $[Na_\phi]$ $10^{-3}$ | $[D_\sigma]$ $10^{-3}$ | $[Na_\sigma]$ $10^{-3}$ | $\theta$ | $-\Delta G°$, kcal./mol. Mechanism B | $-\Delta G°$, kcal./mol. Mechanism C |
|---|---|---|---|---|---|---|---|
| 70 | 4.13 | 30.11 | 0.0003 | 85.47 | 0.211 | 9.60 | 7.59 |
| | 5.20 | 31.37 | 0.0004 | 85.47 | 0.265 | 9.61 | 7.55 |
| | 5.84 | 32.15 | 0.0005 | 85.47 | 0.298 | 9.62 | 7.52 |
| | 6.55 | 33.01 | 0.0006 | 85.47 | 0.334 | 9.64 | 7.51 |
| | 7.35 | 34.02 | 0.0007 | 85.47 | 0.375 | 9.68 | 7.50 |
| | 8.25 | 35.18 | 0.0008 | 85.47 | 0.421 | 9.71 | 7.49 |
| 80 | 4.13 | 30.11 | 0.0006 | 85.47 | 0.211 | 9.34 | 7.27 |
| | 5.84 | 32.15 | 0.0011 | 85.47 | 0.298 | 9.35 | 7.19 |
| | 6.55 | 33.01 | 0.0013 | 85.47 | 0.334 | 9.36 | 7.17 |
| | 7.35 | 34.02 | 0.0015 | 85.47 | 0.375 | 9.40 | 7.16 |
| | 8.25 | 35.18 | 0.0019 | 85.47 | 0.421 | 9.44 | 7.15 |
| | 9.25 | 36.52 | 0.0023 | 85.47 | 0.472 | 9.50 | 7.15 |
| 90 | 4.13 | 30.11 | 0.0012 | 85.47 | 0.211 | 9.09 | 6.95 |
| | 5.20 | 31.37 | 0.0018 | 85.47 | 0.265 | 9.08 | 6.90 |
| | 5.84 | 32.15 | 0.0022 | 85.47 | 0.298 | 9.08 | 6.87 |
| | 6.55 | 33.01 | 0.0027 | 85.47 | 0.334 | 9.09 | 6.84 |
| | 7.35 | 34.02 | 0.0032 | 85.47 | 0.375 | 9.12 | 6.82 |
| | 8.25 | 35.18 | 0.0040 | 85.47 | 0.421 | 9.16 | 6.81 |

Mechanism B: Dye anions absorbed on specific sites and sodium ions diffusely adsorbed.
Mechanism C: Dye anions and sodium ions diffusely adsorbed.

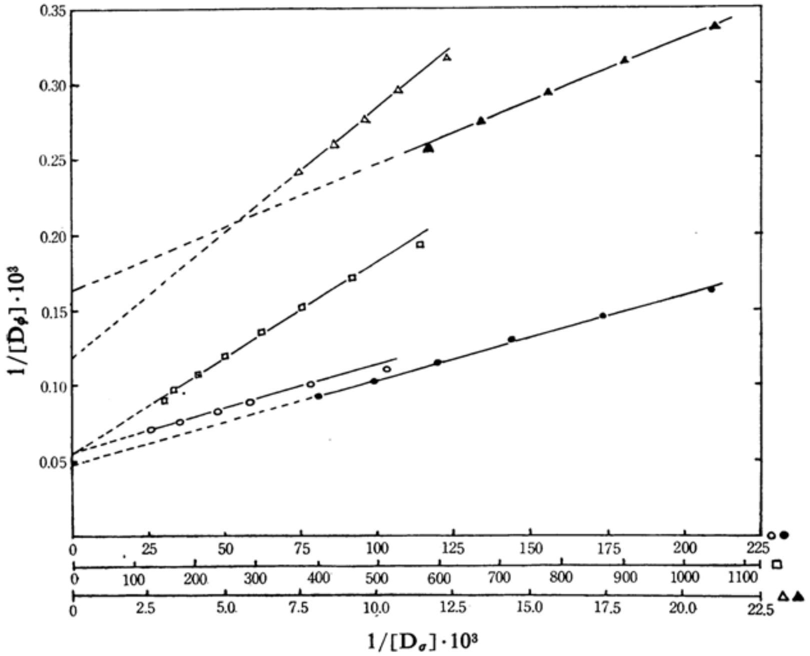

Fig. 5. Plots of $1/[D_\phi]$ and $1/[D_\sigma]$ at 90°C on cotton.

—△— Chlorazol Blue B —▲— Chloramine Blue G
—□— Chloramine Purple 10BC —○— Congo Red
—●— Benzopurpurine 4B

TABLE VII. ADSORPTION OF DYE MIXTURES BY CELLOPHANE SHEET (2 g./l. NaCl)

| Temp. °C | $F_\phi$ g. ions/kg. $\times 10^{-3}$ | $F_\sigma$ g. ions/l. $\times 10^{-6}$ | $F'_\sigma$ g. ions/l. $\times 10^{-6}$ | $F_c$ g. ions/l. $\times 10^{-6}$ | $G_\phi$ g. ions/kg. $\times 10^{-3}$ | $G_\sigma$ g. ions/l. $\times 10^{-6}$ | $G'_\sigma$ g. ions/l. $\times 10^{-6}$ | $G_c$ g. ions/l. $\times 10^{-6}$ | $G_\sigma/F_\sigma$ | $G_c/F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 70 | 3.40 | 9.78 | 3.29 | 6.49 | 0.40 | 8.90 | 2.36 | 6.54 | 0.91 | 1.0 |
| | 2.87 | 9.91 | 2.0 | 7.90 | 0.51 | 10.91 | 2.90 | 8.0 | 1.10 | 1.0 |
| | 1.56 | 9.75 | 0.52 | 9.23 | 1.32 | 19.95 | 9.08 | 10.87 | 2.05 | 1.18 |
| | 0.72 | 9.92 | 0.14 | 9.78 | 2.34 | 39.61 | 19.1 | 20.51 | 3.99 | 2.09 |
| | 0.44 | 9.92 | 0.08 | 9.84 | 3.18 | 59.77 | 30.0 | 29.77 | 6.02 | 3.03 |
| | 0.29 | 10.01 | 0.04 | 9.97 | 3.92 | 79.75 | 42.0 | 37.75 | 7.97 | 3.78 |
| 90 | 1.87 | 9.74 | 6.20 | 3.5 | 0.10 | 4.98 | 1.5 | 3.5 | 0.51 | 1.0 |
| | 1.72 | 9.77 | 5.25 | 4.52 | 0.18 | 7.48 | 2.9 | 4.6 | 0.77 | 1.0 |
| | 1.63 | 9.64 | 4.7 | 4.9 | 0.30 | 10.02 | 4.9 | 5.1 | 1.04 | 1.04 |
| | 0.71 | 10.01 | 1.2 | 8.8 | 1.02 | 39.83 | 18.9 | 20.9 | 3.98 | 2.37 |
| | 0.51 | 9.94 | 0.77 | 9.17 | 1.53 | 59.63 | 30.9 | 28.6 | 6.00 | 3.13 |
| | 0.37 | 9.90 | 0.51 | 9.4 | 1.94 | 79.60 | 42.12 | 37.5 | 8.04 | 3.99 |

dye and fibre at low concentrations may be due both to adsorption on sites of high activity and to steric factors which prevent the dye molecules trapped in the network of cellulose from passing from the fibre phase to the solution phase.

When the affinities of direct cotton dyes for cellulose are to be determined, the main parameters required are the activity of dye in the fibre and in the dyebath. Affinity can be represented by the equation:

$$-\Delta G^\circ = \boldsymbol{R}T \ln a_\phi - \boldsymbol{R}T \ln a_\sigma \qquad (1)$$

where $\boldsymbol{R}$ is the gas constant; $T$, the absolute temperature of dyeing; $a_\phi$, the activity of dye in fibre, and $a_\sigma$, the activity of dye in an aqueous solution. If the dye is assumed to be completely ionised in a solution and if the activity coefficient is considered to be unity, the activity of the dye in solution can be represented by the product of the ionic concentration of the dye anions and sodium ions in the solution, and

$$-\Delta G^\circ = \boldsymbol{R}T \ln a_\phi - \boldsymbol{R}T \ln\, [\mathrm{D}_\sigma]\, [\mathrm{Na}_\sigma]^z \qquad (2)$$

where $[\mathrm{D}_\sigma]$ and $[\mathrm{Na}_\sigma]$ are the ionic concentrations of dye anions and sodium ions in the solution at equilibrium (g. ions/l.) and $z$ is the valency of the dye. For assigning a value to the activity of dye in the cellulose phase, a choice of a suitable function to represent the activity will depend on the mechanism of dyeing which is postulated. If the dye is assumed to be completely ionised in the substrate, the activity of dye in the fibre will vary depending on which of the following three thermodynamic mechanisms is operative during the dyeing:

A. Both the dye anions and sodium ions are adsorbed on specific sites in the fibre in a monomolecular layer and are not subjected to interference, either electrical or otherwise, from the adjacent adsorbed anions.

B. Only the dye anions are adsorbed on specific sites, while the sodium ions are diffusely adsorbed.

C. Both the dye anions and sodium ions are attracted to the fibre-solvent interphase and there is a possibility of formation of a multimolecular layer. Vickerstaff[12] has considered these three thermodynamic approaches for expressing the activity of dye in the fibre phase and has developed appropriate equations for the calculation of activity in the fibre and of affinity values for each of these mechanisms.

Until now only mechanism C could be considered and tested because in the other two mechanisms it was essential to know the exact amount of dye required to form a monolayer in the fibre substance. Peters and Vickerstaff[3] adopted the mechanism of diffused adsorption for both dye anions and gegenions; this mechanism necessitated the use of the volume term $V$, which represents the volume of the surface of the fibre substance which takes part in the dyeing. The validity of this term has, however, been questioned by Preston, Mhatre and Narasimhan,[13] by Nishida[14] and by Horiki[15]. It was, therefore, thought desirable to test the alternative approach of expressing the activity of a direct dye in a fibre substance as the fraction of the total sites occupied at a specific stage of equilibrium dyebath adsorption. From the knowledge of the saturation value of a direct dye for cotton obtained with

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[12] T. Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyd, London (1954), pp. 106-111.

[13] J. M. Preston, S. H. Mhatre and K. I. Narasimhan, *J. Soc. Dyers Colourists*, **65**, 17 (1949).

[14] K. Nishida, *J. Soc. Textile Cellulose Ind. Japan*, **7**, 539 (1951).

[15] Y. Horiki, This Bulletin, **33**, 974 (1960).

precision from the determination of the heat of dyeing at different concentrations of adsorbed dye in the fibre, the two mechanisms, A and B, could be investigated. When mechanism A is applied to the results of the present study, it is found that it is not valid, the slopes of the plots correlating $(z+1)\log\theta_D/(1-\theta_D)$, where $\theta_D$ is the fraction of total sites occupied by dye anions, with $\log[D_\sigma][Na_\sigma]^z$ are far from unity (Table III), and the calculated affinity values are not at all consistent. This is because the dyebath contains both dye and electrolyte; therefore, the total number of sodium ions present in the fibre would not only be equal to those required for maintaining electrical neutrality but would also be equal to the sum of sodium ions surrounding dye anions in an equivalent number and to those arising from the electrolyte present in the fibre phase in equilibrium with the solution phase, according to the Donnan membrane equilibrium.

When mechanism B is considered in connection with the results of the present sudy, under different temperatures and conditions of dye concentration in the bath, plots correlating $\log\theta_D/(1-\theta_D)\cdot[Na_\phi]^z/V^z$ with $\log[D_\sigma][Na_\sigma]^z$ are linear, except for Chlorazol Blue B, Chlorazol Blue G and Chlorazol Orange RN, with slopes close to unity (Figs. 6–8 and Table III), and the affinity values are consistent (Tables IV–VI). $[Na_\phi]$ is the ionic concentration of dye anions in the fibre phase (g. ions/kg.); it can be determined by means of the Donnan equilibrium between sodium ions and chloride ions in the fibre and in the external solution according to the equation derived by Peters and Vickerstaff.3) $V$ is the surface volume in l./kg. dry fibre, which is taken to be 0.3 l./kg. for cotton. In the case of Congo Red, Benzopurpurine 4B and Benzopurpurin 10B, the plots correlating the activity of dye in the fibre to that in the solution are closer to unity, and the affinity values agree more closely with one another when mechanism B is considered than is the case when the treatment of Marshall and

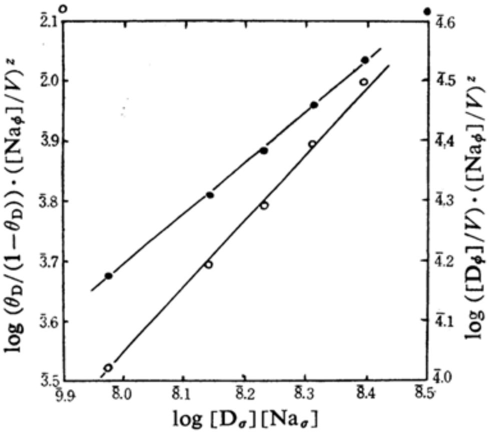

Fig. 6. Plots of log activity of dye in fibre and in bath for Benzopurpurine 4B on cotton at 80°C (5 g./l. NaCl).
—○— Dye ions adsorbed on specific sites and sodium ions diffusely adsorbed
—●— Dye ions and sodium ions diffusely adsorbed

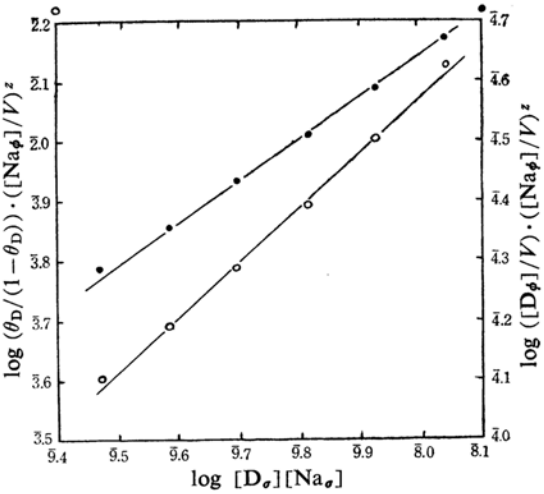

Fig. 7. Plots of log activity of dye in fibre and in bath for Benzopurpurine 10B on cotton at 60°C (5 g./l. NaCl).
—○— Dye ions adsorbed on specific sites and sodium ions diffusely adsorbed
—●— Dye ions and sodium ions diffusely adsorbed

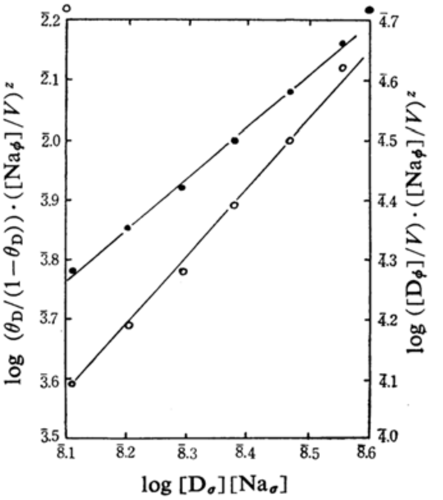

Fig. 8. Plots of log activity of dye in fibre and in bath for Chloramine Purple 10BC on cotton at 90°C (5 g./l. NaCl).
—○— Dye ions adsorbed on specific sites and sodium ions diffusely adsorbed
—●— Dye ions and sodium ions diffusely adsorbed

Peters[16] is considered (mechanism C). The affinity values obtained from the results of dyeing equilibria at different temperatures and the values of the heat dyeing determined from the slopes of the linear plots correlating $\Delta G^\circ/T$ with $1/T$ are given in Table I. It can be seen that the values of the heat of dyeing obtained are close to those obtained from the desorption experiments mentioned earlier, where the method of determining the heat of dyeing does not involve the expression of the activity of the dye in the fibre phase.

The following are the main points which serve to show that the mechanism based on the adsorption of dye anions on specific sites and sodium ions being diffusely adsorbed is more probable for dyeing equilibria with direct dyes on cellulose than that developed by earlier workers based on diffused adsorption for both the ions.

(1) The saturation values which are used to calculate the total number of sites available for dye adsorption in order to determine the activity of the dye in the cellulose substrate are actually obtained from experimental data rather than arbitrarily accepting the volume term, $V$, to fit the experimental results with the postulated theory.

(2) Plots correlating the logarithm of the activity of the dye in the fibre to that in the solution are linear, with slopes approaching unity.

(3) The calculated values of the affinity of a dye are consistent with one another under different conditions of dye concentrations in the bath at each of the dyebath temperatures studied.

(4) Plots correlating $\Delta G^\circ/T$ against $1/T$ are linear, and the values of the heats of dyeing obtained from the slopes of these curves are very close to those obtained from desorption experiments where the treatment used does not involve the expression of the activity of the dye in the fibre.

**The Adsorption of the Dye Mixture.**—Boulton, Delph, Fothergill and Morton,[17] Neale and Stringfellow[18] and Derbyshire and Peters[19] have shown that, with binary mixtures of Chrysophenine G and Chlorazol Sky Blue FF, the equilibrium adsorption of either of the two dyes was reduced when the other dye was present in the dyebath. The main factors which are likely to influence the adsorption of direct dyes from mixtures are competition between different dye anions for available sites in the fibre substance, the effect of each dye in contributing to the surface charge of the cellulose and sodium ion concentrations in the fibre, and interaction between dyes in the solution. As the fibre at a low concentration of adsorbed dye is very far from being saturated, however, competition for available sites is not likely to have much effect. According to Neale and Stringfellow,[18] the effect of each dye on the charge on the fibre surface and on the sodium ion concentration in the fibre is inadequate to explain the reduced adsorption from the mixed dyebath. Thus, the main contribution to the reduction in the dye uptake from a mixed dyebath appears to arise from the interaction of dyes in the solution.

Horiki[15] could explain satisfactorily in a quantitative way the adsorption of Chrysophenine G and Chlorazol Sky Blue FF from a mixed dyebath at 90°C by a cellophane sheet, assuming the formation of 1 : 1 complex and adopting the thermodynamic treatment of Marshall and Peters[16] for equilibrium dyeing. At higher concentrations of Chrysophenine G in the dyebath, however, he could not explain the adsorption behaviour on the basis of the 1 : 1 complex.

In the present study, in order to explain the behaviour of Chrysophenine G and Chlorazol Sky Blue FF when applied from a mixed dyebath, the data given by Horiki[15] have been considered and the saturation values and affinity values for these two dyes in cellophane have been determined by the desorption experiments mentioned before. Assuming that the thermodynamic treatment mentioned before is valid in the case of mixtures also, the effective dyebath concentration of each dye which would effect a specific equilibrium adsorption on cellophane can be calculated from the equation:

$$-\Delta G^\circ = \boldsymbol{RT} \ln \theta_D/(1-\theta_D)\cdot[\mathrm{Na}_\phi]^z/V^z \\ -\boldsymbol{RT} \ln [\mathrm{D'}_\sigma]\,[\mathrm{Na}_\sigma]^z \qquad (3)$$

where $[\mathrm{D'}_\sigma]$ is the effective dyebath concentration of a particular dye (g. ions/l.), when the affinity values of the dyes at a particular temperature and the saturation values of cellophane for these dyes are known. From the knowledge of the effective dyebath concentration of each dye under different concentrations of combinations and at different temperatures, the amount of each dye in the mixture which is ineffective in dyeing can be obtained and the types of complexes of these two dyes likely to be formed under different conditions can be predicted. These results for the dyeing temperatures of 70 and 90°C have been

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[16] W. J. Marshall and R. H. Peters, *J. Soc. Dyers Colourists*, **63**, 446 (1947).

[17] J. Boulton, A. E. Delph, F. Fothergill and T. H. Morton, *J. Textile Inst.*, **24**, P113 (1933).

[18] S. M. Neale and W. A. Stringfellow, *J. Soc. Dyers Colourists*, **59**, 241 (1943).

[19] A. N. Derbyshire and R. H. Peters, ibid., **72**, 268 (1956).

recorded in Table VII, where $F_\phi$ and $G_\phi$ represent the concentrations of Chlorazol Sky Blue FF and Chrysophenine G in cellophane at equilibrium (g. ions/kg.), $F_\sigma$ and $G_\sigma$ are the equilibrium dyebath concentrations of Chlorazol Sky Blue FF and Chrysophenine G in a mixture dyebath (g. ions/l.), $F'_\sigma$ and $G'_\sigma$ are the effective dyebath concentrations of Chlorazol Sky Blue FF and Chrysophenine G (g. ions/l.) as calculated from Eq. 3 and $F_c$ and $G_c$ are the dyebath concentrations of Chlorazol Sky Blue FF and Chrysophenine G ineffective in adsorption because of the interaction of dyes in the mixture (g. ions/l.) (they correspond to $(F_\sigma - F'_\sigma)$ and $(G_\sigma - G'_\sigma)$ respectively). The affinity values of Chlorazol Sky Blue FF for cellophane at 70 and 90°C have been calculated as 8.9 and 7.9 kcal./mol. respectively; the corresponding figures for Chrysophenine G are 6.0 and 5.6 kcal./mol. The saturation values of Chlorazol Sky Blue FF and Chrysophenine G for cellophane as obtained from the measurements of the heats of dyeing are 0.01512 g. ions/kg. dry cellophane and 0.02647 g. ions/kg. dry cellophane respectively. $V$, the volume term of the cellulose phase in cellophane, is considered to be 0.45 l./kg., a figure also used by Marshall and Peters[16] for the calculation of affinity values.

It can be seen from the results of Table VII that the experimental data for the adsorption of these dyes from a mixed dyebath at 70 and 90°C can be explained on the basis of the formation of a 1 : 1 complex between these two dyes up to the stage where the ratio of the amount of Chlorazol Sky Blue FF to that of Chrysophenine G is less than 1 : 2, but at higher concentrations of Chrysophenine G, complexes other than 1 : 1 (namely, 1 : 2, 1 : 3 and 1 : 4) appear to be formed in the dyebath. The types of complexes formed for the same ratio of Chlorazol Sky Blue FF to Chrysophenine G as starting dyebath concentrations appear to be the same at both 70 and 90°C. These results are in agreement with those recorded by Derbyshire and Peters,[19] who, from calorimetric measurements of the magnitude of the heats of interaction between Chrysophenine G and Chlorazol Sky Blue FF, have indicated the possibility of the formation of a considerable proportion of complexes richer in Chrysophenine G in the presence of an excess of this dye in an aqueous solution. These workers have also shown that the adsorption spectrum of a mixture of these two dyes in an aqueous solution is not the same as the sum of the spectra of its constituents and that, even at 90°C, the formation of a 1 : 1 complex takes place in the aqueous solution to an appreciable extent. In agreement with the deductions obtained in the present study from the equilibrium adsorption measurements of these two dyes from a mixed dyebath and the subsequent calculation of the effective dyebath concentration, these workers showed that, when an excess of Chrysophenine G was present in the dyebath, for a constant proportion of Chlorazol Sky Blue FF, the absorption maxima of Chlorazol Sky Blue FF shifted to longer wavelengths, this shows that the formation of higher complexes does take place to a certain extent under these dyebath conditions.

In conclusion, from the results of the present study it may be noted that the thermodynamic treatment developed by Daruwalla and D'Silva[4] is valid for a number of direct cotton dyes with different chemical constitutions and different aggregation behaviours. The affinity values obtained with the present treatment with all the dyes studied are higher than those obtained by adopting the treatment of Marshall and Peters.[16] It is rather difficult, however, to state which of these two sets of values may be considered to represent the true values. Nevertheless, it appears that the values obtained by adopting the thermodynamic treatment developed in the present study, values which are based on experimentally-determined value for the activity of dye in the fibre as calculated from the fraction of the total sites occupied, are likely to be more representative. Futhermore, the thermodynamic treatment used in the present study also explains in a semiquantitative way the equilibrium adsorption behaviour on cellulose of Chrysophenine G and Chlorazol Sky Blue FF when they are applied from mixed dyebaths.

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