*Physico-Chemical Studies on Dyeing Process. I. Theory of Dyeing Equilibrium and Half Dyeing Time of Direct Cotton Dyes on Viscose Rayon**

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The rate of dyeing is subjected to the slow diffusion of dye into the fibre. Neale et. al. measured this rate under the condition that the liquid yarn ratio is infinite. In this case, the outer surface of yarn spontaneously adsorbs the dye corresponding to the dyeing equilibrium. At the same time, the slow diffusion begins to penetrate the yarn, but the dye concentration of the outer surface is constant, the dye diffused into the yarn being supplied at once from the bath. The rate determining process of dyeing is the slow diffusion into the inner part of a fibre. Meanwhile the slow diffusion is affected by the adsorption amount at the outer surface. To study the rate of dyeing, the dyeing equilibrium should be, therefore, known. As for the latter, Vickerstaff et al.[1] studied it both theoretically and experimentally for the case of the liquid yarn ratio is assumed to be infinite.

Boulton et al.[2] defined the "half dyeing time" to compare the rate of dyeing. That is the time required to absorb one half of the equilibrium amount. The experimental determination of the half dyeing time is done under a rather small liquid yarn ratio of 40: 1, and the results are dependent on the equilibrium exhaustion ratio. The theoretical justification on the half dyeing time has not yet been done.

Theory of Dyeing Equilibrium in Finite Liquid Yarn Ratio

In this paper, the dyeing equilibrium of direct cotton dye on viscose rayon is mainly studied. In this case, dye may be assumed to migrate into the capillary gap or miceller interspace. The volume of dye bath per 1 g. of yarn is assumed to be v (l./g.), and the volume of capillary gap per 1 g. of yarn to be V (l./g.). The liquid yarn ratio v was 40 (cc./g.) in Boulton's experiment, and usually much more larger, that is,

$$v \geqq 40\times10^{-3}\ (\text{l./g.}). \tag{1}$$

The volume of capillary gap is according to Marshall and Peters[3], for viscose rayon,

$$V=0.27\times10^{-3}\sim0.46\times10^{-3}\ (\text{l./g.}). \tag{2}$$

The dye molecule discussed here contains z Na atoms and dissociates in solution as follows:

$$\text{DNa}_z \rightleftarrows z\text{Na}^+ + \text{D}^{z-} \tag{3}$$

where D^{z-} is dye anion. In the dye bath, NaCl may be added. The concentration of dye ion, Na^+ ion and Cl^- ion is expressed as [D], [Na], and [Cl] (mol./l.) for solution, and [Dϕ], [Naϕ], and [Clϕ] for fibre phase, respectively. Assuming the absorption amount of dye per 1 g. of fibre as x (g./g. fibre),

$$[\text{D}\phi]=x/MV \tag{4}$$

where M is the molecular weight of dye. The standard chemical potentials of all ions are expressed as $\mu_0(\text{D})$, $\mu_0(\text{Na})$, $\mu_0(\text{Cl})$, $\mu_0(\text{D}\phi)$, $\mu_0(\text{Na}\phi)$, $\mu_0(\text{Cl}\phi)$, and activity coefficients as f_{D}, f_+, f_-, f^ϕ_{D}, f^ϕ_+, and f^ϕ_-. Then the free energy of the total system, F, is

$$\begin{aligned}F=&v[\text{D}]\mu_0(\text{D})+v[\text{D}]RT\ln f_{\text{D}}[\text{D}]\\&+v[\text{Na}]\mu_0(\text{Na})+v[\text{Na}]RT\ln f_+[\text{Na}]\\&+v[\text{Cl}]\mu_0(\text{Cl})+v[\text{Cl}]RT\ln f_-[\text{Cl}]\\&+V[\text{D}\phi]\mu_0(\text{D}\phi)+V[\text{D}\phi]RT\ln f^\phi_{\text{D}}[\text{D}\phi]\\&+V[\text{Na}\phi]\mu_0(\text{Na}\phi)+V[\text{Na}\phi]RT\ln f^\phi_+[\text{Na}\phi]\\&+V[\text{Cl}\phi]\mu_0(\text{Cl}\phi)+V[\text{Cl}\phi]RT\ln f^\phi_-[\text{Cl}\phi].\end{aligned} \tag{5}$$

As for the electrical interaction of fibre surface and dye ion, Gilbert and Rideal[4] introduced the electrical potential difference ψ at the surface, to explain the combination of protein and inorganic acid. But this is less important to discuss than the interaction of direct cotton dye with cellulose. Assuming that the change of electrical potential during the dyeing process may be rather small, it is included in the term μ_0, in this paper.

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* A part of this paper was presented before the Discussion of Colloid Chemistry held by this Society at Nov. 1954.

[1] Vickerstaff, "The Physical Chemistry of Dyeing", 2nd. rev. ed. (1954), p. 191-256.

[2] J. Boulton and B. Reading, *J. Soc. Dyers and Colourists*, **50**, 381 (1934); J. Boulton, ibid., **54**, 268 (1938); **60**, 5 (1944).

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

[4] G.A. Gilbert and E.K. Rideal, *Proc. Roy. Soc.*, **A 182**, 335 (1944).

Since the total amount of dye ion is constant,

$$vN_o=v[\mathrm{D}]+V[\mathrm{D}\phi] \tag{6}$$

where N_o is the initial concentration of dye in the bath. Then, this gives, with Eq. (4), the formula to calculate the adsorption amount:

$$x=MV[\mathrm{D}\phi]=Mv(N_o-[\mathrm{D}]). \tag{7}$$

From the constancy of Na and Cl,

$$vN_s+zvN_o=v[\mathrm{Na}]+V[\mathrm{Na}\phi] \tag{8}$$

and

$$vN_s=v[\mathrm{Cl}]+V[\mathrm{Cl}\phi] \tag{9}$$

where N_s is the initial concentration of NaCl in the bath. From the condition of electrical neutrality for dye bath and for the fibre phase,

$$z[\mathrm{D}]+[\mathrm{Cl}]=[\mathrm{Na}] \tag{10}$$

and

$$z[\mathrm{D}\phi]+[\mathrm{Cl}\phi]=[\mathrm{Na}\phi] \tag{11}$$

are obtained.

With these equations and Eq. (5), the free energy may be expressed as a function of [Na] and [D]. Then, using the equilibrium condition that the partial differentiation of F by [Na] and [D] are respectively equal to zero, the dyeing equilibrium is formulated. Using the further assumption that

$$\mu_0(\mathrm{Na}\phi)-\mu_0(\mathrm{Na})=\Delta\mu(\mathrm{Na})=0 \tag{12}$$

$$\mu_0(\mathrm{Cl}\phi)-\mu_0(\mathrm{Cl})=\Delta\mu(\mathrm{Cl})=0 \tag{13}$$

that is Na^+ and Cl^- do not have any especial affinity to the fibre, Donnan's equation for membrane equilibrium:

$$f_+f_-[\mathrm{Na}][\mathrm{Cl}]=f_+^\phi f_-^\phi[\mathrm{Na}\phi[\mathrm{Cl}\phi] \tag{14}$$

is obtained from one of the equilibrium conditions

$$\partial F/\partial[\mathrm{Na}]=0. \tag{15}$$

Nearly every theoretical study ever proposed is assuming Eq. (14) a priori. It should be, however, emphasized that this equation is correct merely when Na^+ and Cl^- have no affinity to the fibre.

Then, from the other equilibrium condition

$$\partial F/\partial[\mathrm{D}]=0 \tag{16}$$

and Eq. (13) and Eq. (14),

$$\begin{aligned}\Delta\mu(\mathrm{D})&=\mu_0(\mathrm{D}\phi)-\mu_0(\mathrm{D})\\&=RT\ln\left\{\frac{f_\mathrm{D}[\mathrm{D}]\{f_+[\mathrm{Na}]\}^z}{f_\mathrm{D}^\phi[\mathrm{D}\phi]\{f_+^\phi[\mathrm{Na}\phi]\}^z}\right\}\end{aligned} \tag{17}$$

is obtained. On the other hand, from Eqs. (11) and (14),

$$[\mathrm{Na}\phi]=(z/2)[\mathrm{D}\phi]+\sqrt{(z^2/4)[\mathrm{D}\phi]^2+[\mathrm{Na}][\mathrm{Cl}]} \tag{18}$$

is obtained, if $f=1$.

At the infinite liquid yarn ratio,

$$[\mathrm{Na}]=N_s+zN_o \tag{19}$$

and

$$[\mathrm{Cl}]=N_s\,. \tag{20}$$

Marshall and Peters[3] and Peters and Vickerstaff[5] used these equations in Eq. (18) to calculate the value [Naφ], and showed that Eq. (17) is supported by experimental data. Vickerstaff[1] also showed that the equation of Willis, Warwicker, Standing and Urquhart[6] and that of Hanson, Neale and Stringfellow[7] are, respectively, derived as special cases of Eqs. (17) and (18).

In the case of finite liquid yarn ratio, [Na] and [Cl] both depend on [Naφ], so that Eqs. (19) and (20) can not be used. Using Eqs. (7)–(11) and (14), [Naφ] is strictly calculated as a function of [Dφ], N_s, and N_o. Even when the liquid yarn ratio is finite,

$$f^2\equiv f_+^\phi f_-^\phi/f_+f_-\gg(V/v)^2 \tag{21}$$

$$(V/v)N_o\ll f^2[\mathrm{D}\phi]\equiv f^2(v/V)(N_o-[\mathrm{D}]) \tag{22}$$

and

$$z[\mathrm{D}\phi]/2\gg(V/v)N_s/f^2 \tag{23}$$

are satisfied, referring to Eqs. (1) and (2). Under these approximations,

$$\begin{aligned}[\mathrm{Na}\phi]&\fallingdotseq(z/2)[\mathrm{D}\phi]\\&\quad+\sqrt{(z^2/4)[\mathrm{D}\phi]^2+N_s(N_s+zN_o)/f^2}\end{aligned} \tag{24}$$

is obtained. This equation for finite liquid yarn ratio is coincident with Eq. (18), using Eqs. (19) and (20) for infinite ratio. Under the approximation of Eqs. (21)–(23), the value [Na] for finite liquid yarn ratio is, however,

$$\begin{aligned}[\mathrm{Na}]&\fallingdotseq N_s+zN_o-(z/2)(V/v)[\mathrm{D}\phi]\\&\quad-(V/v)\sqrt{(z^2/4)[\mathrm{D}\phi]^2+N_s(N_s+zN_o)/f^2}\end{aligned} \tag{25}$$

which does not coincide with Eq. (19) for infinite ratio.

In a special case where

$$(z/2)[\mathrm{D}\phi]\gg N_s/f \tag{26}$$

Eq. (25) becomes

$$[\mathrm{Na}]\fallingdotseq N_s+z[\mathrm{D}] \tag{27}$$

which also does not coincide with Eq. (19). from Eqs. (27), (7) and (8),

$$[\mathrm{Na}\phi]\fallingdotseq z[\mathrm{D}\phi] \tag{28}$$

is obtained. Let the eqilibrium adsorption amount be x_∞ and the concentration of dye in the bath be N_∞, then under the condition of Eq. (26),

$$\left.\begin{aligned}&\log x_\infty=\alpha+\left(\frac{1}{z+1}\right)X\\&X=\log N_\infty+z\log(N_s+zN_\infty)\\&\alpha=-\frac{0.4343}{z+1}\frac{\Delta\mu(\mathrm{D})}{RT}-\log h\\&\qquad+\log MV-\frac{z}{z+1}\log z\end{aligned}\right\} \tag{29}$$

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5) R.H. Peters and T. Vickerstaff, *Proc. Roy. Soc.*, A **192**, 292 (1948).

6) H.F. Willis, J.O. Warwicker, H.A. Standing and A.R. Urquhart, *Trans. Faraday Soc.*, **41**, 506 (1945).

7) J. Hanson, S.M. Neale and W.A. Stringfellow, ibid., **31**, 1718 (1935).

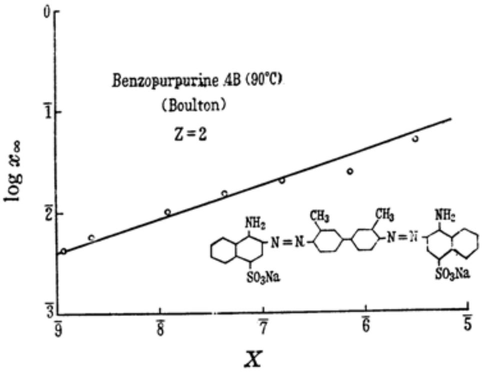

Fig. 1. Absorption of Benzopurpurine 4B on viscose rayon yarn in finite liquid yarn ratio (by Boulton).

is obtained. Fig. 1 shows the varification of Eq. (29). Plots in the figure are calculated by the present author from the Boulton's data[2] for the dyeing of Cautould's 150/27 viscose rayon yarn by Benzoperpurine 4B in finite liquid yarn ratio (40 : 1). The straight line in the figure is drawn so as to satisfy the theoretical inclination, $1/(z+1)=1/3$. The agreement with the experimental value is good. From this straight line,

$$\alpha=0.60 \tag{30}$$

is obtained. Assuming

$$h\equiv\left(\frac{f_{\mathrm{D}}^{\phi}(f_{+}^{\phi})^{z}}{f_{\mathrm{D}}(f_{+})^{z}}\right)^{\frac{1}{z+1}}\fallingdotseq 1 \tag{31}$$

and, for viscose rayon[3],

$$V=0.45\times10^{-3}\ (\mathrm{l./g.}) \tag{32}$$

the following is obtained:

$$\begin{aligned}&-\Delta\mu(\text{Benzoperpurine 4B})\\&=6.4_5\ \text{kcal./mol. (at 90°C)}\end{aligned} \tag{33}$$

Hanson and Neale[8] measured the dyeing equilibrium of the same Benzoperpurine 4B on viscose rayon (cellophane film, in this case), at infinite liquid yarn ratio. In this case, however, the ratio (NaCl/dye) was much greater than in the case of Boulton, so that the assumption (26) and Eq. (29) cannot be used. In this case, [Na] and [Naϕ] should be calculated from Eqs. (19) and (24), and inserted into Eq. (17). The latter may be rewritten as

$$\left.\begin{aligned}&\log[\mathrm{D}\phi][\mathrm{Na}\phi]^{z}=\beta+\log[\mathrm{D}][\mathrm{Na}]^{z}\\&\beta=-0.4343\Delta\mu/RT-(z+1)\log h\end{aligned}\right\} \tag{34}$$

under the assumption of

$$f=1. \tag{35}$$

The result of calculation is shown in Fig. 2, where the straight line is drawn so as to

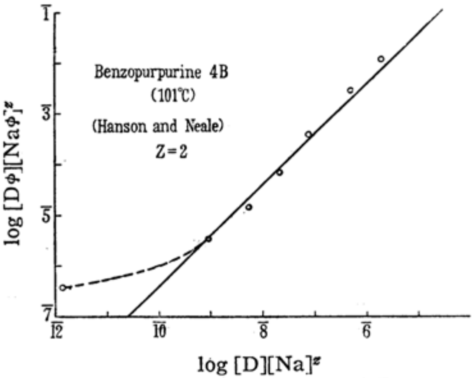

Fig. 2. Dyeing equilibrium of Benzopurpurine 4B on cellophane in infinite liquid yarn ratio (by Hanson and Neale).

satisfy the theoretical gradient in Eq. (34). From this straight line,

$$\beta=3.59 \tag{36}$$

is obtained. Using the second equations of (34) and Eq. (31), Eq. (36) is recalculated to

$$\begin{aligned}&-\Delta\mu(\text{Benzoperpurine 4B})\\&=6.2\ \text{kcal./mol. (at 101°C)}\end{aligned} \tag{37}$$

which is in good agreement with Eq. (33).

The dyeing equilibrium of Sky Blue FF (Chicago Blue 6B) on viscose rayon measured by Boulton[2] at finite liquid yarn ratio, and by Hanson and Neale[8] and Marshall and Peters[3] at infinite liquid yarn ratio are plotted in Fig. 3. Eqs. (24), (25) are used for finite liquid yarn ratio, and Eqs. (18), (19) and (20) are used for infinite ratio. V is assumed to be 0.45×10^{-3} (l./g.). As shown in the figure, $\log[\mathrm{D}\phi][\mathrm{Na}\phi]^z$ shows linear relationship to $\log[\mathrm{D}][\mathrm{Na}]^z$, but the slope of the line is greater than the theoretical value,

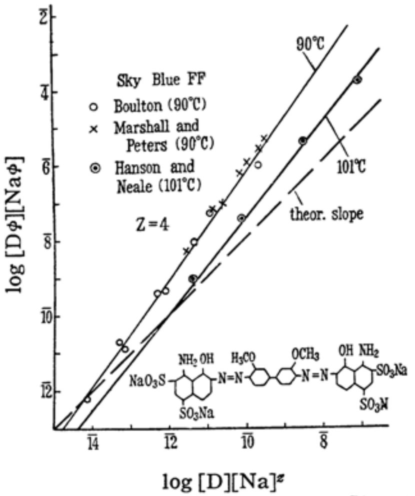

Fig. 3. Dyeing equilibrium of Sky Blue FF on viscose rayon.

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[8] J. Hanson and S.M. Neale, *Trans. Faraday Soc.*, 30, 386 (1934).

unity, shown in Eq. (34). The straight lines are:

$$\log[\mathrm{D}\phi][\mathrm{Na}\phi]^4 = 7.92 + 1.42\log[\mathrm{D}][\mathrm{Na}]^4 \text{ for } 90^\circ\mathrm{C} \tag{38}$$

and

$$\log[\mathrm{D}\phi][\mathrm{Na}\phi]^4 = 4.97 + 1.24\log[\mathrm{D}][\mathrm{Na}]^4 \text{ for } 101^\circ\mathrm{C}. \tag{39}$$

It is noticeable that both data for infinite and finite liquid yarn ratio are on the same straight line of Eq. (38) for 90°C, as shown in Fig. 3.

Marshall and Peters3) attributed the deviation of the slope of the straight lines from the theoretical value to the aggregation of dye ions. They thought that the standard chemical potential $\Delta\mu(\mathrm{D})$ is dependent on the concentration, assuming the activity coefficients always equal to unity. This is, however, not correct, since the activity coefficients largely deviate from unity when the aggregation sets up. While, the standard chemical potential of adsorption may be assumed unchanged, considering that the adsorbed dye is in equilibrium with monomolecularly dispersed dye, and that the effective concentration of the latter should be properly expressed using the activity coefficient. Details of the concentration dependence of the activity coefficient of dye is not known, yet but it is known for soaps. Soap belongs to the same colloidal electrolyte as dye. Curves such as in Fig. 4 are obtained for the osmotic coefficient, g. If the concentration C is smaller than C_c, the activity coefficient of soap follows the Debye-Hückel equation, and is nearly equal to unity. C_c is the critical micelle concentration. When the concentration is greater than C_c, the micelle is formed and the osmotic coefficient decreases rapidly. When the concentration is greater than C_t, the osmotic coefficient becomes constant, or increases gradually. Data on some soaps are shown in Fig. 5⁹⁾, where $\log g$-$\log C$ relation is nearly linear at the concentration range from C_c to C_t.

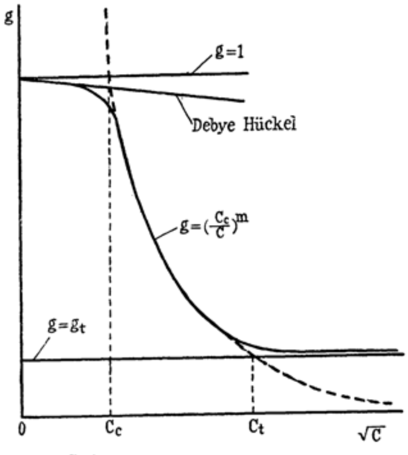

Fig. 4. Schematic explanation of osmotic coefficient-concentration relation for micelle colloids.

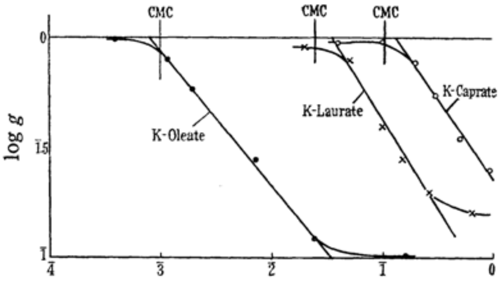

Fig. 5. $\log g$-$\log C$ relation for some soap solutions.

The osmotic coefficient g is nearly equal to the mean activity coefficient, $\bar{f}$,

$$\bar{f} = (\prod_i f_i^{\nu_i})^{\frac{1}{\sum_i \nu_i}} \tag{40}$$

In the case of dye shown in Eq. (3), the mean activity coefficient is written as

$$\bar{f} = (f_\mathrm{D}\cdot f_+^{z})^{\frac{1}{z+1}} \tag{41}$$

Then, it is assumed that the activity coefficient of dye may be assumed to be the same as that of soap, that is:

$$\bar{f} = \begin{cases} 1 & (C < C_c) \\ (C_c/C)^m & (C_c < C < C_t) \\ f_t & (C_t < C) \end{cases} \tag{42}$$

where f_t is a constant. It is generally accepted that the micelle is seldom formed at 90°C or so, and the micelle forming tendency of dye is not so conspicuous as that of soap. Then,

$$\bar{f} \simeq 1. \tag{43}$$

On the other hand, the concentration of dye in fibre phase, $[\mathrm{D}\phi]$, is usually 50–2000 times greater than that in solution, [D]. Therefore, it may correspond to the case of $C > C_t$, so

$$\bar{f}^{\phi} = \{f_\mathrm{D}^{\phi}\cdot(f_+^{\phi})^{z}\}^{\frac{1}{z+1}} = f_t \tag{44}$$

and

$$h = \bar{f}^{\phi}/\bar{f} = f_t = \text{const.} \tag{45}$$

Then the slope of the linear relation in $\log[\mathrm{D}\phi][\mathrm{Na}\phi]^z \sim \log[\mathrm{D}][\mathrm{Na}]^z$ diagram is equal to the theoretical value, unity, but the value of $\Delta\mu(\mathrm{D})$ cannot be obtained without knowing the value of f_t, Benzoperpurine 4B (Fig. 1 and 2) will be the case, and the values of $\Delta\mu(\mathrm{D})$ of Eqs. (33) and (37) are apparent values.

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9) J.W. Mc Bain, "Colloid Science" (1950), p. 245-253.

On the other hand, Sky Blue FF has 4 sulphonic groups and it may be more difficult for it to form micelle than Benzoperpurine 4B having 2 sulphonic groups. Then, the concentration of Sky Blue FF in fibre phase may correspond to the concentration range of $C_c < C < C_t$. Then,

$$h = (C_c / C^{\phi})^m \tag{46}$$

where C_c is a constant and C^{ϕ} is

$$C^{\phi} = \{[\mathrm{D}^{\phi}][\mathrm{Na}^{\phi}]^z\}^{\frac{1}{z+1}}. \tag{47}$$

Eq. (34) should be rewritten as

$$\log\,[\mathrm{D}^{\phi}][\mathrm{Na}^{\phi}]^z = \gamma + \left(\frac{1}{1-m}\right)\log\,[\mathrm{D}][\mathrm{Na}]^z$$

$$\gamma = -\frac{0.4343}{1-m}\,\frac{RT}{\Delta\mu} - \frac{m}{1-m}(z+1)\log C_c\,. \tag{48}$$

To satisfy the observed relations, Eqs. (38) and (39), the following values

$$m = \begin{cases} 0.30 & \text{for } 90^\circ\mathrm{C} \\ 0.19 & \text{for } 101^\circ\mathrm{C} \end{cases} \tag{49}$$

should be adopted. For soap solutions, $m = 0.6$–0.8 is obtained from Fig. 5, while the value for dye may be smaller than these values, since dye forms micelle with more difficulty. Therefore, the values cited in Eq. (49) are acceptable.

Theory on the Rate of Dyeing

The rate of dyeing of Benzoperpurine 4B and Sky Blue FF on viscose rayon yarn (Coutauld's 150/27) was measured by Boulton[2)] at 90°C using purified dyes. The liquid yarn ratio was 40. The exhaustion ratio E was measured as a function of time t (min.). The exhaustion ratio was defined by

$$E = (C_o - C)/C_o = (N_o - N)/N_o \tag{50}$$

where C_o (g./l.) or N_o (mol./l.) is the initial dye concentration and C or N is the dye concentration after t (min.) The exhaustion ratio after sixteen hours was assumed as the equilibrium exhaustion ratio, E_∞, and the time required to reach $E = E_\infty/2$ is named as half dyeing time, T. The half dyeing time was measured by Boulton for many dyes but theoretical treatment was not tried.

To find a simple empirical relationship, the ratio of adsorption amount ξ, that is

$$\xi = E/E_\infty = x/x_\infty \tag{51}$$

is plotted against the ratio of time to the half dyeing time, that is,

$$\tau = t/T. \tag{52}$$

In Fig. 6, ξ-τ relationship from Boulton's data is shown. For the dyeing of Benzoperpurine 4B on viscose rayon, dye concentration varied 0.02–2.6 millimole, NaCl concentration 1.1–40 millimole, and equilibrium adsorption amount 4.2–25 mg./g. yarn, and for Sky Blue FF on the same yarn, dye concentration varied 0.005–0.14 millimole/l., NaCl concentration 4–43 millimole/l., and equilibrium adsorption amount 0.2–7.4 mg./g. yarn. All plots fall on a single curve, irrespective of the sorts of dyes and the dyeing conditions were very widely different. The simple empirical equations obtained are,

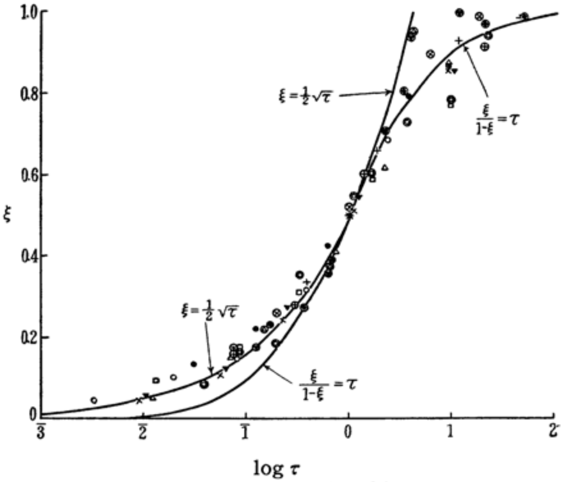

Fig. 6. ξ-τ relationship.

$$\xi = \tfrac{1}{2}\sqrt{\tau} \quad \text{for } \tau < 1 \tag{53}$$

and

$$\xi/(1-\xi) = \tau \quad \text{for } \tau > 1 \tag{54}$$

Then, suppose that fibre has many capillary gaps and the total volume of them is V (l./g. yarn). The shape of the gap is assumed for the simplicity as a capillary of uniform diameter. At the opening of the capillary, the dyeing equilibrium is immediately established, and the dye diffused into the inner part of the capillary is readily supplied from the dye bath, so that the concentration at the opening N_o^{ϕ} (mol./l.) is a function of the dye bath composition only. At the initial stage of the diffusion, N_o^{ϕ} is approximately constant, and the depth of the penetration of dye is smaller than the depth of the capillary, L. Then, the equation of Fürth[10)] is used:

$$\left.\begin{aligned} y^2/t &= D/\varphi(q) \\ q &= N_o^{\phi}/N^{\phi} \end{aligned}\right\} \tag{55}$$

where the concentration of dye ion at the distance y (cm.) from the opening is N^{ϕ} and diffusion coefficient is D, and time is t. $\varphi(q)$ is the function of q only and

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10) R. Fürth, *Phys. Z.*, **26**, 719 (1925); *Kolloid-Z.*, **41**, 300 (1927).

$$1/q=1-\frac{2}{\sqrt{\pi}}\int_0^{\frac{1}{2\sqrt{\varphi}}} e^{-\xi^2}\mathrm{d}\xi \tag{56}$$

Using these, the concentration gradient at time t and location y becomes,

$$\frac{\mathrm{d}N^{\phi}}{\mathrm{d}y}=-\frac{N^{\phi}_{\circ}}{\sqrt{\pi}\sqrt{D}}\frac{1}{\sqrt{t}}e^{-\frac{1}{4\varphi}}\,. \tag{57}$$

Then, using the relation[11] that,
when $y\rightarrow 0$, and therefore $q\rightarrow 1$,
then $\varphi\longrightarrow\infty$ (58)
the concentration gradient at the opening is

$$\left(\frac{\mathrm{d}N^{\phi}}{\mathrm{d}y}\right)_0=-\frac{1}{\sqrt{\pi}\sqrt{D}}\frac{N^{\phi}_{\circ}}{\sqrt{t}}\,. \tag{59}$$

The rate of dyeing $\mathrm{d}x/\mathrm{d}t$ is,

$$\frac{\mathrm{d}x}{\mathrm{d}t}=-\frac{DAM}{1000}\left(\frac{\mathrm{d}N^{\phi}}{\mathrm{d}y}\right)_0$$

$$=\frac{A\sqrt{D}}{\sqrt{\pi}}\cdot\frac{MN^{\phi}_{\circ}}{1000}\frac{1}{\sqrt{t}} \tag{60}$$

where A is the sum of the cross section of capillary (cm^2/g. yarn) and adsorption amout x is expressed in g. dye/g. yarn, and the factor 1000 is used to rewrite the $N^{\phi}_{\circ}$ in mol./l. to mol./cc.

At the initial stage of diffusion, $N^{\phi}_{\circ}$=constant, so that

$$x=\frac{2A\sqrt{D}MN^{\phi}_{\circ}}{1000\sqrt{\pi}}\sqrt{t} \tag{61}$$

is obtained. Then the definition of the half dyeing time,

$$x=x_{\infty}/2 \quad \text{when } t=T \tag{62}$$

is used with Eq. (61) and

$$\xi=x/x_{\infty}=\tfrac{1}{2}\sqrt{\tau} \quad \text{where } \tau=t/T \tag{63}$$

is obtained. This is equal to Eq. (53). Then,

$$N^{\phi}_0=x_t/MV \tag{64}$$

where x_t is the equilibrium adsorption amount (g./g.) when an infinitesimal amount of fibre (that means the surface only of the fibre) is dipped into the dye bath, whose composition is that at time t. Moreover, V (l./g.) is

$$V=AL\times10^{-3}. \tag{65}$$

Using these equations, the half dyeing time is,

$$T=\frac{\pi L^2}{16D}Q^2$$

$$Q=x_{\infty}/x_t \tag{66}$$

At the infinite liquid yarn ratio,

$$x_t=x_{\infty} \tag{67}$$

so that the value of Q is equal to unity, and from Eq. (66),

$$T=0.197\ L^2/D \tag{68}$$

is obtained. On the other hand, Neale, Stringfellow, Hanson, Andrew and Johnston[12] used the equation by Hill[13]

$$\left.\begin{aligned}\xi=1-\frac{8}{\pi^2}\Big\{&e^{-\frac{\pi^2D}{4b^2}t}+\frac{1}{9}e^{-\frac{9\pi^2D}{4b^2}t}\\&+\frac{1}{25}e^{-\frac{25\pi^2D}{4b^2}t}+\ldots\ldots\Big\}\end{aligned}\right\} \tag{69}$$

where b is a half of the thickness of a cellophane film. The relation between ξ and Dt/b^2 calculated from Eq. (69) is shown in the first two columns of Table I. Since the time at which $\xi=0.5$ is the half dyeing time, T, so from Table I,

$$DT/b^2=0.197$$

that is

$$T=0.197\ b^2/D \tag{70}$$

is obtained. If it is assumed that the value of L corresponds to b, Eq. (70) is equal to Eq. (68). Then,(Dt/b^2) is recalculated to τ, by the equation

$$\tau=t/T=\frac{Dt}{0.197\,b^2} \tag{71}$$

as shown in the third column of Table I, and ξ is calculated by Eq. (63), as shown in the fourth column of the table. The results are in good agreement with that by Hill, as far as $\xi\leq0.7$. Therefore, the complicated Hill's equation is replaced by a simpler equation (63) without any loss of accuracy as far as $\xi\leq0.7$.

TABLE I

Dt/b^2	ξ Eq. (69)	τ Eq. (71)	ξ Eq. (63)
0.0085	0.1	0.0432	0.104
0.0315	0.2	0.160	0.200
0.049	0.25	0.249	0.250
0.0725	0.3	0.369	0.303
0.125	0.4	0.635	0.398
0.197	0.5	1.000	0.500
0.286	0.6	1.452	0.602
0.404	0.7	2.05	0.715
0.472	0.75	2.40	(0.775)
0.570	0.8	2.90	(0.850)
0.843	0.9	4.28	(1.03)
1.13	0.949	5.74	—
1.35	0.971	6.85	—
1.80	0.990	9.13	—
2.25	0.997	11.42	—

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[11] M. Nakagaki, *Bull. Chem. Soc. Japan*, **23**, 104 (1950).

[12] S.M. Neale and W.A. Strigngfellow, *Trans. Faraday Soc.*, **29**, 1167 (1933); J. Hanson and S.M. Neale, ibid., **30**, 386 (1934); D.H. Andrew and J. Johnston, *J. Am. Chem. Soc.*, **46**, 640 (1924).

[13] A.V. Hill, *Proc. Roy. Soc.*, B **104**, 39 (1928).

At the finite liquid yarn ratio, Q is not equal to unity. When the equilibrium exhausion is greater, and equilibrium dye bath concentration is smaller, then, x_∞ becomes smaller and Q becomes smaller. Therefore, T becomes smaller when the E_∞ is greater, as shown by Boulton. As shown before, the dyeing equilibrium of Benzoperpurine 4B on viscose rayon yarn is expressed by Eq. (29). The dye concentration of dye bath N should be used in place of N_∞, for x_t. Then, replacing N and N_∞ by E and E_∞ using Eq. (50),

$$Q=\frac{x^\infty}{x_t}=\frac{(1-E_\infty)^{\frac{1}{z+1}}\left(\frac{N_s}{N_o}+z-zE_\infty\right)^{\frac{z}{z+1}}}{(1-E)^{\frac{1}{z+1}}\left(\frac{N_s}{N_o}+z-zE\right)^{\frac{z}{z+1}}} \tag{72}$$

is obtained. At the initial stage of dyeing, E is nearly equal to zero, so the value of Q is

$$Q\fallingdotseq(1-E_\infty)^{\frac{1}{z+1}}\left(\frac{N_s}{N_o}+z-zE_\infty\right)^{\frac{z}{z+1}}\Big/\left(\frac{N_s}{N_o}+z\right)^{\frac{z}{z+1}} \tag{73}$$

The relation between Boulton's half dyeing time and the Q value, calculated from Eq. (73), is shown in Fig. 7. As a rough approximation T is proportional to Q^2, though the plot for $T=24.9$ min. deviates from the linearity. The results of Hanson and Neale[8] showed that the apparent diffusion coefficient becomes smaller when the salt concentration is smaller. The case of $T=24.9$ corresponds to this case, so that the deviation from the linearity will be explained from the decrease of apparent diffusion coefficient, which is often attributed to the variation of the surface potential at the fibre-water interface. From the inclination of the straight line in Fig. 7,

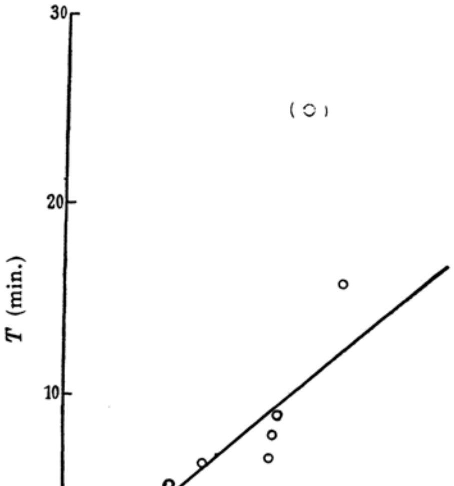

Fig. 7. T-Q^2 relation for benzopurpurine 4B.

$$L^2/16D=16.6\,(\text{min.}) \tag{74}$$

is obtained. As already said about Eq. (70), L should be approximately equal to the radius of the single fibre. The latter is

$$r=1.1\times10^{-3}\,\text{cm.} \tag{75}$$

for 150/27 yarn, (a single yarn is 5.5 deniers), assuming that the density of fibre is about 1.5. Using this value in L of Eq. (74), diffusion coefficient is,

$$D=1.4\times10^{-8}\ (\text{cm}^2/\text{min.}) \tag{76}$$

This is approximately equal to the value by Hanson and Neale[8].

Summary

The theory of dyeing equilibrium is treated generally. On the way of derivation, it is emphasized that the Donnan's equation,

$$f_+f_-[\text{Na}][\text{Cl}]=f_+^\phi f_-^\phi[\text{Na}^\phi][\text{Cl}^\phi]$$

is correct only when Na^+ and Cl^- have no affinity to the fibre. An equation expressing dyeing equilibrium is obtained for finite liquid yarn ratio, and compared to the equation by Vickerstaff for infinite liquid yarn ratio. Moreover, data for both finite and infinite liquid yarn ratio could be plotted on the same straight line according to the newly derived equation. The deviation of the inclination of the straight line from the theoretical value is attributed to the deviation of the activity coefficient from unity. The latter was assumed as analogous to that of soap, and a reasonable conclusion could be obtained.

On the theory of dyeing rate, all data from widely different dyeing conditions are brought into a simple relation

$$x/x_\infty=\frac{1}{2}\sqrt{t/T}\quad\text{when}\quad t<T$$

using the half dyeing time T proposed by Boulton. This equation was justified theoretically, and it was shown that Hill's complicated equation is replaced by this simple equation, without loss of accuracy, as far as $x/x_\infty\leq0.7$. Then, Boulton's relation, that

the half dyeing time becomes longer when the equilibrium exhaustion ratio is smaller, is justified theoretically. The apparent diffusion coefficient in fibre agrees with that of Hanson and Neale.

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