Relations Between Viscoelastic Parameters of Hydrophobic Fiber and Dyeing with Disperse Dyes

S. D. SUPANEKAR, *Bombay Textile Research Association,*
Lal Bahadur Shastri Marg, Ghathopar, Bombay 86, India
and E. H. DARUWALLA, *Department of Chemical Technology,*
University of Bombay, Bombay 19, India

Synopsis

Experimental evidence is presented to show that the kinetics of dyeing of hydrophobic fibers with disperse dyes can be represented by an equation of the same form as the well-known equation giving creep in fibers. A mechanism is proposed whereby one can regard the dye uptake in the fiber at a constant temperature as a viscoelastic phenomenon in the dye-polymer system. A comparison of these two equations enables the dyeing constants to be interpreted in terms of the viscoelastic parameters of the system. It is also possible to find the upper bounds for the dyeing rate and a condition for rapid dyeing on the same basis.

From a theoretical point of view, dyeing of hydrophobic fibers with nonionic dyes is comparatively simple because, the electrical effects being absent in this system, it would be reasonable to look for a mechanical explanation for the observed dyeing behavior. The kinetics of dyeing of synthetic fiber with disperse dyes have been studied by several workers,[1-3] but the theoretical treatment is neither simple nor very satisfactory. In the following, an attempt has been made to relate dyeing behavior with viscoelastic properties of the dye–polymer system. A close analogy is found to exist between dye uptake by the substrate and the strain developed in the model dye–polymer system. The results obtained reveal that the viscoelastic model has a wider domain of applicability than hitherto believed.

Diffusion of nonionic disperse dyes in polymer substrate fiber has been considered to consist of the following stages[4]: (a) transport of the dye through the dyebath on to the substrate surface; (b) adsorption of dye at the fiber surface; and (c) diffusion of dye within the substrate.

As dye cannot diffuse in "solid" fiber, the concept of capillary in the fiber substance has been introduced. If this concept is accepted, it naturally obliterates the concept of the fiber surface and stage (b) above; viz., adsorption at the surface loses much of its significance. Furthermore, the presence of capillary walls also interferes with the principal axiom in the derivation of diffusion equation, viz., that the concentration gradient is the

motive force in the diffusion phenomenon. This also conflicts with requirements that D be a constant in the solution of Hill's equation,[5]

$$\frac{C_t}{C_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{\alpha^2_n} e^{-\frac{D\alpha_n^2 t}{r^2}} \tag{1}$$

which is frequently employed to determine the diffusion coefficient. In eq. (1), C_t is the amount of dye on the fiber at time t, D is the diffusion coefficient, r is the radius of the fiber, and α_n is the root of the zero order Bessel function $J_0(\alpha_n) = 0$. In spite of these limitations, it is found that the kinetic data obtained in the present study with certain model disperse dyes of related structures can be satisfactorily represented by a canonical scheme:

$$\frac{C_t}{C_\infty} = 1 - A e^{-Bt}. \tag{2}$$

In fact, eq. (2) is the truncated form of eq. (1) when only the first term in the summation is retained. Under such conditions, eq. (1) becomes

$$\frac{C_t}{C_\infty} = 1 - 0.692\, e^{\frac{-5.782\, Dt}{r^2}} \tag{3}$$

Milicevic[2] has reached similar conclusions except that he has considered the value of A in eq. (2) to be unity. As indicated in the following, this makes considerable difference in the physical characteristics of the system. Dyeing rates have been obtained in the present study by dyeing from an aqueous dispersion of the dye, cellulose triacetate, polyamide, and polyester fibers at 98°C from an infinite bath.[6] ("Infinite bath" indicates conditions of dyebath where the liquor to material ratio is very high, 10,000:1). Dyes used were closely related in chemical structure. Experimental values of C_t/C_∞ have been transformed to log $(1 - C_t/C_\infty)$ and fitted with time t by the least-squares procedure. Correlation coefficient obtained in case of cellulose triacetate and nylon are the best possible ones. Even for polyester fiber, though slightly low, correlations are still very good. The values A and B are given in Table I, and the validity of eq. (2) can be considered as established. When A in eq. (2) has a value less than unity initially, i.e., at $t = 0$,

$$C_0 = C_\infty(1 - A). \tag{4}$$

This equation represents some instantaneous dye uptake, and the corresponding kinetic profile is as given in Figure 1a. This situation, though surprising, is by no means unique in physical phenomena, e.g., use of Dirac's δ function to describe instantaneous changes. Experimentally, eq. (4) cannot be disproved because the range of zero in practice is always a small interval.
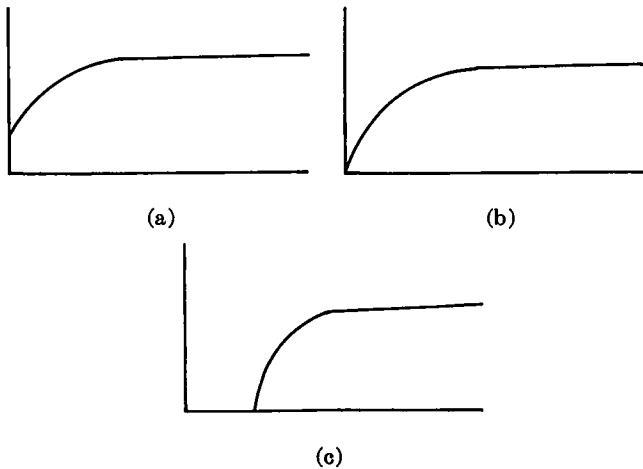
Fig. 1. Kinetic profiles for dyeing; (a) $A < 1$: (b) $A = 1$: (c) $A > 1$.

When $A > 1$, the situation can be readily reconciled. The natural interpretation in this instance is that dyeing commences after a lapse of time, given by

$$t_0 = \frac{\log A}{B}. \tag{5}$$

This profile has the appearance given in Figure 1c. However, as indicated in the following, the viscoelastic explanation of the dyeing behavior precludes the values of $A \geq 1$.

Viscoelastic models employed for a textile fiber are mainly developed for stress–strain properties of fibers; and in this connection, the work of Eyring and his co-workers[7,8,9] is of special interest. These investigators have put forward a three-element model consisting of two springs and a dashpot as a satisfactory concept to represent the viscoelastic behavior of textile fibers. Either of the arrangements of these elements (Fig. 2) leads to similar results. More precisely, given k_1 and k_2 for the model of Figure 2a, the values of k_1' and k_2' depending on k_1 and k_2 could be found such that the strain developed in both the models is the same at any time t. In this sense the two models are equivalent. The main object of the work of these investigators was to study the load elongation and creep properties of fibers over the entire range; and the investigators found it necessary to introduce a non-Newtonian behavior in their analysis *via* the viscous element. It has been postulated by the investigators that the strain ϵ in the system is proportional to the hyperbolic sine of the stress μ acting upon it. When μ is small or the time for which it acts is short, as in the present case, this system goes over to a simpler Newtonian one. For such a simple system, if k_1 and k_2 are the spring constants and β is the dashpot constant, and when

TABLE I
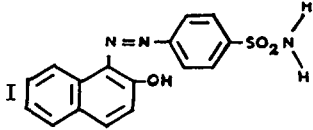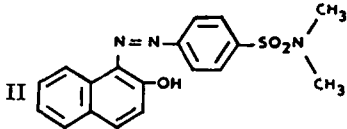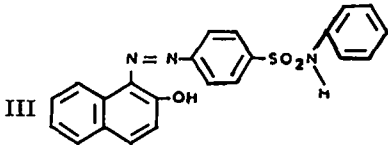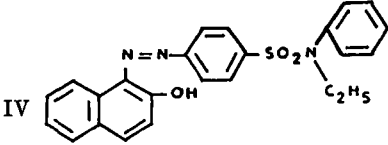Kinetic Data for the Dyeing Systems.   Dyeing Temperature 98°C
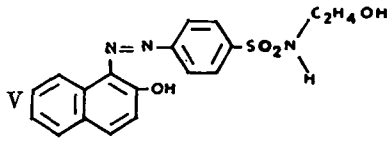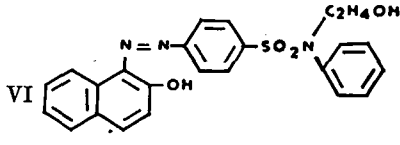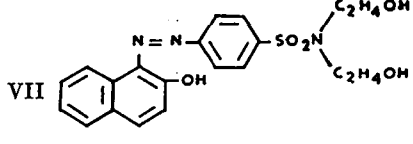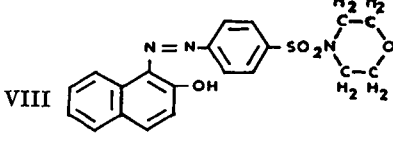
Dye no.	Cellulose triacetate		
	Corr. coeff.	A	$B \times 10^2$
I	−0.99	0.80	1.61
II	−0.99	0.79	1.66
III	−0.99	0.83	1.36
IV	−0.99	0.82	1.24
V	−0.99	0.81	1.48
VI	−0.99	0.81	1.49
VII	−0.99	0.71	5.23
VIII	−0.99	0.85	4.42

TABLE I (*continued*)

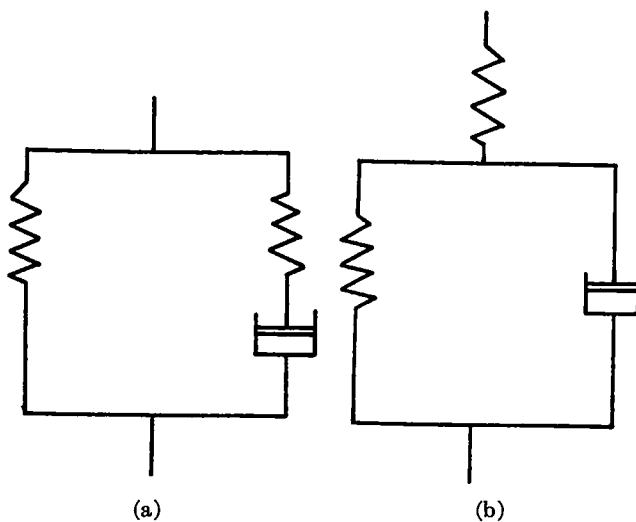|	Nylon				Polyester		
	Corr. coeff.	A	$B \times 10^2$		Corr. coeff.	A	$B \times 10^2$
	−0.99	0.82	1.14		−0.97	0.97	1.57
	−0.99	0.86	1.54		−0.96	1.04	1.64
	−0.99	0.84	0.927		—	—	—
	−0.99	0.84	0.909		−0.97	0.96	1.56
	−0.98	0.83	1.00		—	—	—
	−0.99	0.84	1.09		−0.97	0.95	1.55
	−0.99	0.75	3.78		−0.97	0.96	1.56
	−0.99	0.75	2.20		−0.97	0.96	1.56

Fig. 2. Viscoelastic model for fiber; (a) Maxwell unit and a spring in parallel: (b) Kelvin-Voigt unit with a spring in series.

a constant stress μ is applied at time $t = 0$, the strain ϵ developed in the system depends on the time and is given by the following equation[10]:

$$\epsilon = \epsilon_t = \frac{\mu}{k_2}\left(1 - \frac{k_1}{k_1 + k_2}\, e^{-\frac{k_1 k_2 t}{\beta(k_1 + k_2)}}\right). \tag{6}$$

The resemblance between eqs. (2) and (6) is very striking and should not be considered as fortuitous.

The viscoelastic model for a textile fiber is postulated to account for the fact that fiber substances are composed of long-chain molecules; and as some of them are too firmly attached by secondary bonds, slippage is retarded.[7]   According to the kinetic theory of elasticity, these act as pure springs, and other molecules which are not so strongly bonded and which may contain loops undergo stretching and slippage.   These segments correspond to the Maxwell unit in Figure 2a.   As each of these units actually represent the whole distribution of molecular elements, the characteristic constants in the proposed scheme represent average values. When a fiber is introduced into a dyebath, the inner polymer structure becomes subjected to a stress, and on account of springlike elements present, some instantaneous strain will develop.   This strain will increase as the Maxwellian dashpot moves.

In this context, the strain may be identified with the opening up of the chain segments, and such opening or unfolding would facilitate the passage of dye molecules and also make additional dye sites accessible to them. This process cannot continue indefinitely because the adsorbed dye molecule would load the segment to which it gets attached, and it would then cause certain immobilization of the latter.   Such loadings would retard

the subsequent unfolding of polymer chains, and after a certain stage dye uptake will tend to level off. Thus, according to this concept, dye uptake C_t would be proportional to the strain ϵ_t developed in the fiber at any instant, and these two processes would become concurrent and parallel. Under such conditions, it is possible to correlate the viscoelastic and dyeing parameters. Clearly, a certain amount of phase lag between strain developed and the dye uptake cannot be ruled out. Thus, C_t may be proportional not to ϵ_t but to ϵ_t' where $t' < t$. However, until this fact is established through some sophisticated experiments, there appears to be no reason to adopt this less elementary hypothesis.

On the basis of the simpler hypothesis, a comparison of eqs. (2) and (6) yields

$$A = \frac{k_1}{k_1 + k_2} \tag{7}$$

$$B = \frac{k_1 k_2}{\beta(k_1 + k_2)} \tag{8}$$

$$C_\infty = \frac{\mu}{k_2} \tag{9}$$

The quantity A governs the irreversible energy losses in the viscoelastic displacement.[9] It may be noted from eq. (7) that the value of A is always less than unity, and subsequently the possibilities represented in Figures 1b and 1c may be excluded from the present scheme. When $k_1 > k_2$, the fiber will generally have poor orientation and/or a low degree of polymerization. As the ratio k_1/k_2 approaches ∞, A tends to 1. Under this situation, it could be inferred from the model given in Figure 2b (which now is better suited for interpretation) that the three-element model gives way to the more familiar Kelvin-Voigt model (Fig. 3).

The second parameter B is the reciprocal of the relaxation time for the system. Thus, the two properties, viz., dyeing behavior and viscoelasticity, are interconnected and their parameters are closely related.

An interesting deduction follows from eqs. (7) and (8). Assuming that the two spring constants differ in value, e.g., $k_1 < k_2$, say,

$$B = \left(\frac{k_1}{\beta}\right)\left(\frac{k_2}{(k_1 + k_2)}\right) < \frac{k_1}{\beta}$$

$$B = \left(\frac{k_2}{\beta}\right)\left(\frac{k_1}{(k_1 + k_2)}\right) \leq \frac{k_2}{2\beta}$$

and thus,

$$B < \min. \frac{(k_1, k_2)}{\beta}$$

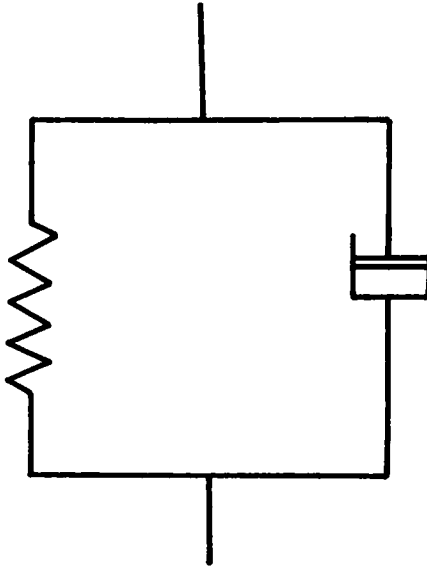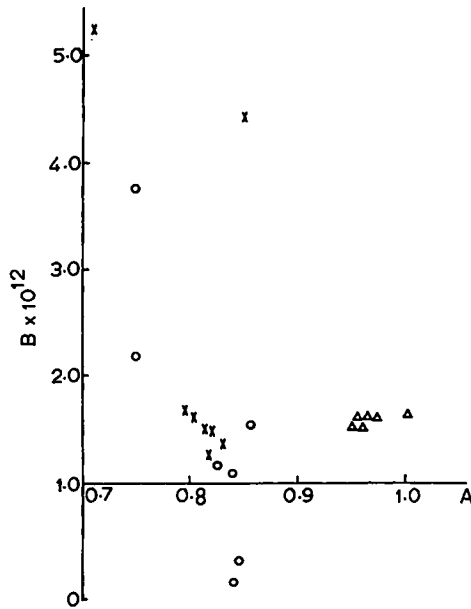$$B \leq \max. \frac{(k_1, k_2)}{2\beta}.$$

Fig. 3. Kelvin-Voigt unit.

Fig. 4. Plot of B vs. A for different dye–fiber systems; (X) cellulose triacetate: (O) polyamide: (Δ) polyester.

From eq. (8) it follows that for a given k_1, B increases with k_2 and will be maximum when k_2 has the maximum possible value. Because of the symmetry of eq. (8) in k_1 and k_2, a similar conclusion can be drawn with regard to k_1. Hence, for fastest dyeing, k_1, k_2 should be as large as possible.

Thus, if it is possible to control these parameters, desirable conditions for rapid dyeing could be achieved.   It is clear that the viscoelastic parameters are determined both by dye as well as by fiber structure.   In case of a highly oriented and crystalline fiber, the chain structure will be more rigid and less prone to variation by the dye.   This is borne out by the results given in Figure 4, in which B is plotted against A.   In case of cellulose triacetate and nylon, B varies with $A;$ but for the polyester fiber, B remains practically constant.

In the treatment mentioned above, temperature dependence of the system is not taken into account, nor is any direct evidence for the validity of eqs. (7) and (8) put forth.   Work covering these aspects is in progress and will be reported later.

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