Studies in Disperse Dye Transfer Mechanism in Polyester–Viscose Union at Elevated Temperatures

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Synopsis

The thermofixation process of dyeing polyethylene terephthalate–viscose union fabric with disperse dyes has been experimentally studied with a view to understanding the phenomena of dyeing polyester blends. It is shown how the distribution of a disperse dyestuff changes on the terylene and viscose portions of a union during different stages of dyeing by the thermofixation process. Equilibrium adsorption isotherm and rate curves of adsorption of disperse dyes on the polyester portion of the union have been determined. The nature of staining of the viscose portion of the union with different disperse dyes has been investigated. From the presented typical data it is possible to deduce fairly simple semiempirical rules regarding the phenomena of the thermofixation process of dyeing polyester–viscose union. It is pointed out that it is not possible to derive an exact thermodynamic theory to explain the data and describe the molecular mechanisms in such systems.

INTRODUCTION

The thermofixation process[1,2] is now a well-established dyeing technique and the dyeing of polyester–cellulosic blends by this process is commonly practiced in textile industry. The dye transfer to cellulose acetate, polyester, and polyamide substrate from the vapor phase of dyestuff has been investigated.[3-5] It is also known that dye transfer to the polyester substrate in thermofixation process can take place via the vapor phase of dye.[6] The distribution of a disperse dye in a multilayer of alternate polyester and cotton fabrics has been also examined.[6] The dyeing of polyester–cellulosic materials has been studied from the practical point of view by many workers to examine the problems, e.g., staining of the cellulosic part by disperse dye.[7-19] In this paper, the quantitative data on fixation of a disperse dye on the polyester portion of a blend is presented, with a view to understanding the phenomena of dyeing polyester blends by the thermofixation process.

EXPERIMENTAL

The union fabric used for the present studies contained 40% terylene and 60% viscose. The dyes (I and II) were dispersed under identical conditions using a dispersing agent for 48 hr in a ball mill and were used as such.

I   II
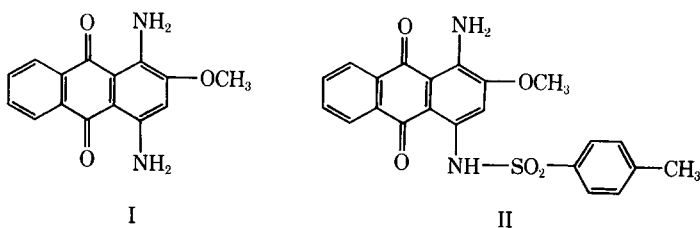
The union fabric was padded with an aqueous dispersion of dyestuff and dried at 120°C for 1 min in a Benz Hot-Air Fixation Unit.[20]   For fixation at elevated temperatures (170°C–205°C) a Benz Hot-Air Fixation Unit or a Wuerz Precision Laboratory Press[21] was used.   For estimation of dye on viscose and terylene portions the warp and weft of the union fabric was first separated by hand.   The fixed dye, $D_T{}^\phi$, on the terylene portion was then extracted with chlorobenzene at reflux and estimated colorimetrically. For estimation of unfixed dye on the terylene portion, $D_T{}^\sigma$, the sample was wetted with water and extracted in cold acetone (0°C–5°C).   The dye on the viscose portion was removed by wetting it first with hot water and then extracting it in cold dimethylformamide.   After dyeing the union, it was soaped in the usual manner with soap and soda at boiling to remove the unfixed dye.   Then the stain on viscose, i.e., dye remaining after soaping of viscose portion, $D_W{}^\sigma$, is estimated as mentioned above.

RESULTS

The deposited dye on the polyester–viscose union, $D_{TV}{}^\sigma$, after padding with an aqueous dispersion of dyestuff and drying, varies with the mangle
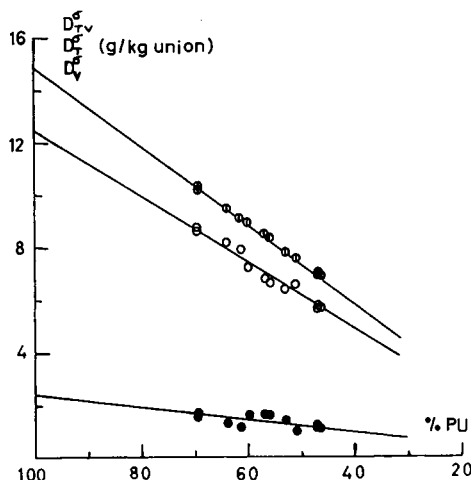

Fig. 1. Dye deposited on terylene–viscose mixed fabric (40:60), $D_{TV}{}^\sigma$, and on its terylene portion, $D_T{}^\sigma$, or viscose portion, $D_V{}^\sigma$, as a function of mangle pickup, PU%. Pad liquor contained 45 g/kg dye I in microdispersed form, i.e., 14.85 g pure dye I pigment per Kg pad liquor: (◑) terylene–viscose mixed fabric; (O) viscose portion; (●) terylene portion.
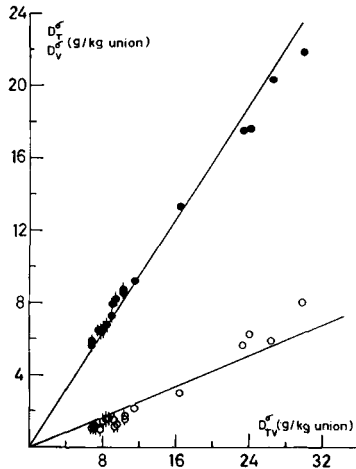
Fig. 2. Distribution of dyestuff I on terylene portion, D_T^{σ}, and viscose portion, D_V^{σ}, of a mixed fabric after padding and drying at 120°C for 1 min. Mangle pressure P varied: ($\bigcirc$) D_T^{σ}; ($\bullet$) D_V^{σ}. (Pad liquor contained 45 g/kg dye I in microdispersed form, i.e., 14.85 g pure dye I pigment per kg pad liquor). Quantity of dyestuff I in pad liquor varied at constant mangle pressure: (O) D_T^{σ}; ($\bullet$) D_V^{σ}.
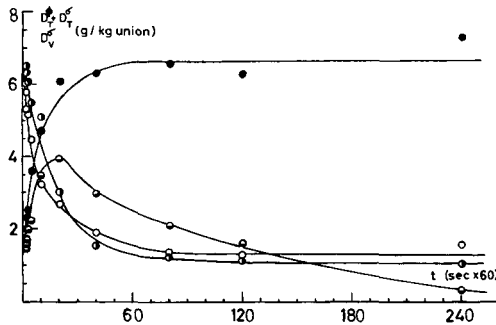

Fig. 3. Comparison of distribution of dyestuff II on terylene portion, $D_T^{\sigma} + D_V^{\phi}$, and on viscose portion, D_V^{σ}, during fixation at 195°C in different fixation units. Precision Laboratory Press: ($\bullet$) terylene portion; (O) viscose portion. Benz Hot-Air Fixation Unit: ($\ominus$) terylene portion; ($\oslash$) viscose portion. (Deposited dye on union fabric D_{TV}^{σ} = 7.78 g/kg union).

pressure P (Fig. 1). The D_{TV}^{σ} on union, as expected, increased as the mangle pressure P decreased. The amount of deposited dye on viscose portion, D_V^{σ}, and on terylene portion, D_T^{σ}, of the union also varies with mangle pressure P in a similar manner. The concentration of deposited dye on viscose portion, D_V^{σ}, is always more than that on polyester, D_T^{σ}, in the union.

The D_{TV}^{σ} can be deposited in different amounts either by varying the mangle pressure P for a constant concentration of dye in the pad bath or by changing dye concentration in the pad bath at a constant P. It is very interesting to note that for a given concentration of deposited dye on union,
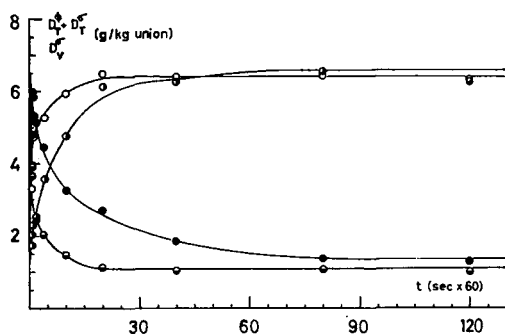
Fig. 4. Comparison of distribution of dyestuff I on terylene portion, $D_T{}^\sigma + D_T{}^\varphi$, and on viscose portion, $D_V{}^\sigma$, of a union fabric with that of dyestuff II during fixation at 195°C in the Precision Laboratory Press. Dye I: (O) terylene portion; (◒) viscose portion. Dye II: (◑) terylene portion; (●) viscose portion. (Concentration of deposited dye I or II on union fabric $D_{TV}{}^\sigma = 7.78$ g/kg union.)
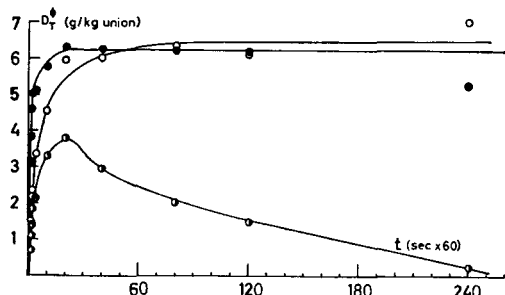

Fig. 5. Fixed dyestuff, $D_T{}^\varphi$, on terylene portion of terylene–viscose union (40:60) as a function of time of fixation t at 195°C. Precision Laboratory Press: (●) dye I; O dye II. Benz Hot-Air Fixation Unit: (◐) dye II. (Concentration of deposited dye I or II on union fabric $D_{TV}{}^\sigma = 7.78$ g/kg union.)

$D_{TV}{}^\sigma$, the distribution of deposited dye on the terylene and viscose portions is always the same and does not seem to depend on the method of deposition (Fig. 2).

Comparison of distribution of dyestuff II on the terylene portion (fixed + unfixed dye, $D_T{}^\varphi + D_T{}^\sigma$) and unfixed dye on the viscose portion, $D_V{}^\sigma$, of a union fabric during fixation at 195°C using the Hot-Air Fixation Unit and Precision Laboratory Press Unit has been made (Fig. 3). Using the Precision Laboratory Press Unit for fixation, the distribution of dye I during dyeing is compared with that of dye II (Fig. 4).

The rates of dye fixation on the terylene portion during thermofixation of terylene–viscose union have also been determined (Fig. 5).

DISCUSSION

On impregnating the polyester–viscose union with aqueous dye dispersion and drying, it is observed that the amount of dye deposited on the viscose portion is always more than that on polyester portion (Fig. 2). This is to

be expected because owing to the hydrophilic nature of the viscose substrate it will absorb more pad liquor during impregnation and also retain more after squeezing on the padding mangle compared to the hydrophobic polyester portion. In addition, it is also known that in case of polyester–cotton blend, water evaporates at the surface of the cotton where most of the dye is deposited.[6,22] Due to the large amount of disperse dye deposition on cotton or the viscose portion in a blend during padding and drying, this problem of staining cotton or viscose portion is encountered especially during the continuous one-bath method of dyeing polyester blends with disperse and reactive dyes by the thermofixation process.[7,8,16−19]

It is evident from Figure 3 that fixation time t plays an important role while dyeing union fabrics in the Hot-Air Fixation Unit. The dye $(D_T{}^\phi + D_T{}^\sigma)$ on terylene portion first increases, attains a certain maximum value, and then decreases, while the unfixed dyestuff on viscose, $D_V{}^\sigma$, decreases and then tends to level off as t is increased. On the other hand, using the Precision Laboratory Press Unit for fixation, the dye $(D_T{}^\phi + D_T{}^\sigma)$ increases rapidly and attains a constant equilibrium value, while $D_V{}^\sigma$ decreases rapidly and levels off with increase in t. The maximum value of $D_T{}^\phi + D_T{}^\sigma$ obtained is more in the Precision Laboratory Press Unit than in the former one. This behavior in the two fixation units is to be expected from the known facts about rate curves[12] (dyestuff II). As the Hot-Air Fixation Unit is open to the atmosphere, the superficially deposited dye from the surface of the union would always sublime in the atmosphere and also the desorption of fixed dye would occur with increase in t. Such a situation does not exist in Precision Laboratory Press Unit, where the sample is almost enclosed between the two heated plates during fixation. It is for this reason that the Precision Laboratory Press Unit was used for experimental work throughout to obtain the physiochemical data, unless mentioned otherwise.

During fixation, the dyestuff is transferred very rapidly from the viscose portion onto the polyester portion, thus changing the distribution of dyestuff between the two fibers in the union. The typical results of distribution for dyestuffs I and II obtained after fixation at 195°C for various times of fixation t are shown in Figure 4. It is interesting to note that the variation in distribution of dyestuff in a polyester–viscose blend depends also on the dyestuff. This is to be expected from the known facts that the vapor pressure of dyestuff II is lower than that of dyestuff I and that the dye transport takes place via the vapor phase of the dyestuff.[6]

The fixed dye on the terylene portion, $D_T{}^\phi$, increases in the beginning and then attains a maximum value $D_{max}{}^\phi$ as t is increased. The rate at which $D_{max}{}^\phi$ is attained would naturally depend on the dyestuff and the fixation unit (Fig. 5). During padding and drying of the terylene–viscose union, it is probable that the deposited dye on viscose portion is present (1) partly on the outermost surface of the viscose fiber and (2) partly in the fine structure of the fiber. It is even possible that part of the dye might have diffused inside the fine structure of viscose fiber during the fixation

step.[6] Most of the dyestuff, however, might be located only in the easily accessible amorphous region of the viscose fiber.   The kinetics of dye fixation on the polyester portion in a union may be controlled by several interrelated factors such as (1) rate of sublimation of dye from the outermost surface of viscose, (2) migration of dye from fine structure of viscose to the outermost surface and then sublimation, (3) diffusion of dye molecules in the vapor phase through the ambient space to reach the polyester portion, (4) rate of adsorption and diffusion of dye molecules from viscose portion into the polyester portion, and (5) adsorption and diffusion of dye already present on the polyester portion.   From this it is evident that the dye transport phenomenon in polyester–viscose union is very complicated and difficult to analyze and to apply diffusion mathematics to this heterogeneous mass transport system.   However if the rate curves are analyzed by plotting $D_T{}^\phi$ against $\sqrt{t}$, it would appear that there are approximately three rates at which the dye is fixed on terylene portion.   The first initial faster rate of dye fixation may be due mainly to factor (5), the second, slower one may be due to factors (1), (3) and (4), and the third, slowest one is likely to be due to factors (2), (3), and (4).

Nevertheless, it is possible to show that the fixed dye on the terylene portion, $D_T{}^\phi$, increases with fixation time t and attains a constant equilibrium value $D_{max}{}^\phi$ depending upon the dye initially present on the union, $D_{TV}{}^\sigma$ (Fig. 6).   The $D_M{}^\sigma$, dye migrated from the viscose portion to polyester portion is shown as a function of dye initially present on the viscose portion $D_V{}^\sigma$ (Fig. 7).   From the shape of the curve in Figure 7, it is clear that the dye migrating from viscose portion, $D_M{}^\sigma$, at equilibrium first increases and then decreases as concentration of dye initially present on viscose portion, $D_V{}^\sigma$, is increased, thus indicating that no migration of dye would probably take place from viscose portion once the polyester portion in the union has reached its saturation stage.

The fixed dye on the terylene portion at equilibrium, $D_{max}{}^\phi$, has been shown to have a definite relation with the unfixed dye on the union fabric, $(D_T{}^\sigma + D_V{}^\sigma)$, (Fig. 8).   Such data are analyzed in a manner analogous to Langmuirs adsorption isotherm by plotting $1/D_{max}{}^\phi$ against $1/(D_T{}^\sigma + D_V{}^\sigma)$ (Fig. 9).   The analogy is, in this instance, of only a formal nature since conditions for the validity of such a relationship are not fulfilled.[23] Nevertheless, it has been shown that when such an isotherm fits a series of experimental results and one does not specify the nature of adsorption, it is still possible to use the same.[24]   The corresponding saturation value for the polyester portion $D_S{}^\phi$ can then be calculated from the intersection of the ordinate for any given temperature.   The temperature dependence of $D_S{}^\phi$ is shown in Figure 10.   From the linear relationship obtained by plotting $\log D_S{}^\phi$ against $1/T$, the apparent value for the heat of solution, $\Delta H°$, of the crystalline dyestuff in the polyester substrate can then be derived from the slope of the line according to van't Hoff's isochor:

$$\Delta H° = -R \left[\frac{d \ln D_S{}^\phi}{d\ (1/T)} \right]_p$$

It is most striking to note that the saturation values $D_S{}^\phi$, obtained for the polyester portion in a manner mentioned above, are identical within the experimental errors with those obtained by (1) repeated padding and thermofixation of the union, and (2) obtained for polyester alone by method already described elsewhere.[6]

Thus $D_S{}^\phi$ does not depend on the fixation method or on the experimental technique by which it is determined, but is a characteristic function of fiber and temperature alone. Further, if the dyestuff vapor is supposed to obey ideal gas laws under the experimental conditions, then the concentration of saturated dye vapor D_{SV} around the polyester portion can be calculated from the equation

$$D_{SV} = \frac{pM}{RT}$$

where p is the saturation vapor pressure of the dyestuff (in atmospheres) at temperature T, M is the molecular weight of the dyestuff, and R is the gas
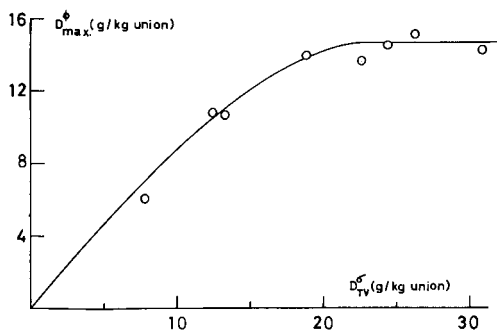
Fig. 6. Fixed dye at equilibrium, $D_{max}{}^\phi$, on terylene portion of union as a function of deposited dye, $D_{TV}{}^\sigma$, on terylene–viscose union (40:60). Precision Laboratory Press; fixation temperature 195°C; dye I.
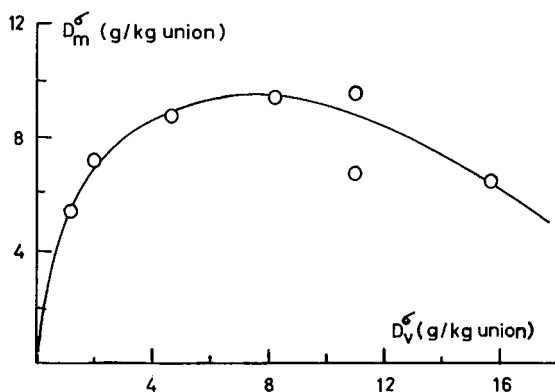
Fig. 7. Migrated dye $D_m{}^\sigma$ from viscose portion to terylene portion as a function of dye initially present on viscose portion, $D_V{}^\sigma$, of union. Precision Laboratory Press; fixation temperature 195°C; dye I.
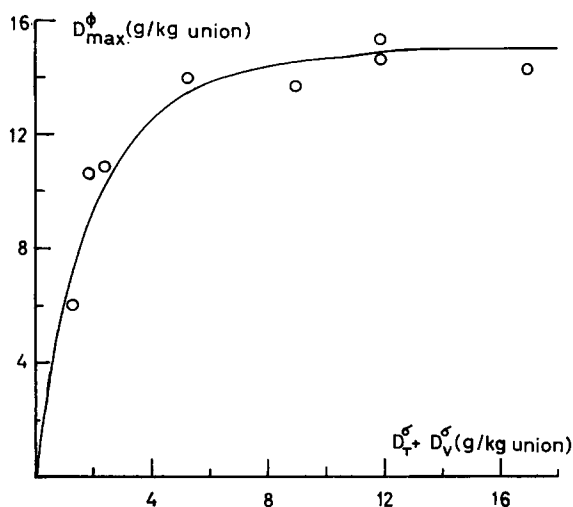
Fig. 8. Fixed dye at equilibrium $D_{max}{}^{\phi}$ on terylene portion as a function of unfixed dye, $D_T{}^{\sigma} + D_V{}^{\sigma}$, on terylene–viscose union fabric. Precision Laboratory Press; fixation temperature 195°C; dye I.
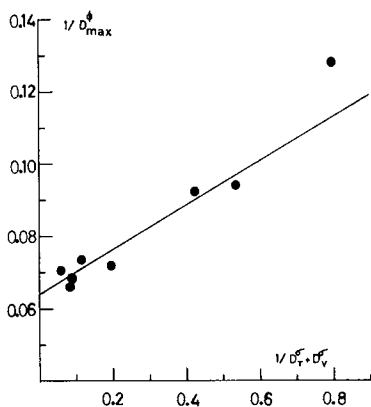

Fig. 9. Analysis of the curve shown in Figure 8 using $(1/D_{max}{}^{\phi}) = \{1/[K'D_s \ (D_T{}^{\sigma} + D_V{}^{\sigma})]\} + (1/D_s{}^{\phi})$. The intersection of the ordinate corresponds to the extrapolated reciprocal fiber-saturation value, $1/D_s{}^{\phi}$, at 195°C for dyestuff I on terylene portion of union. Precision Laboratory Press. (The obtained value of $D_s{}^{\phi}$ will be in g/kg union.)

constant. In addition, if it is further assumed that the distribution isotherm for the dyestuff between the vapor phase and fiber substrate phase is linear,[3] the distribution coefficient K can be calculated from

$$K = \frac{D_s{}^{\phi}}{D_{SV}}.$$

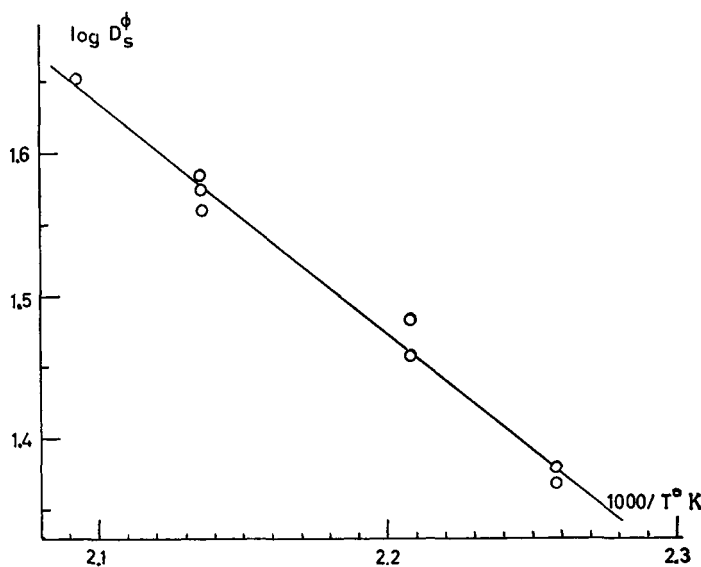The distribution coefficient K is probably related to the change in the

Fig. 10. Temperature dependence of saturation value D_s^ϕ (g/kg terylene) for dye I.
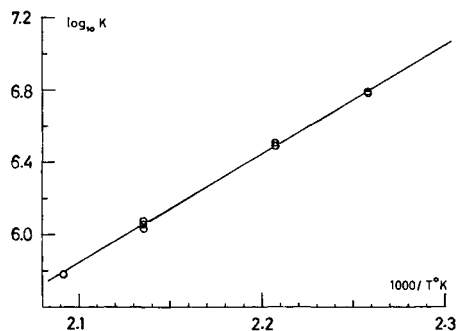

Fig. 11. Distribution coefficient K as a function of temperature for dye I.

apparent Gibbs free energy, ΔG°, for the transfer of one mole of dye from its standard state in vapor to its standard state in the fiber phase.

$$-\Delta G^\circ = RT \ln K = -\Delta H_D^\circ + T\Delta S_D^\circ.$$

It is possible to calculate ΔG° and further the entropy of dyeing, ΔS_D°. Alternatively, if the value of log K is plotted against $1/T$, one obtains a linear relationship (Fig. 11) from the slope of which the heat of dyeing, ΔH_D°, can be calculated.

From a knowledge of the heat of sublimation of dyestuff,[6] ΔH_S°, and the heat of solution of dye in substrate, ΔH°, it is also possible to evaluate ΔH_D° from the difference[25]:

$$\Delta H_S^\circ - \Delta H^\circ = -\Delta H_D^\circ.$$

TABLE I

Apparent Change in Enthalpy of Dyestuff I[a]

		p in mm Hg.
1. $\log p = \dfrac{A}{T} + B$		$A = -7925$ $B = 14.642$
2. Apparent heat of sublimation, ΔH_S°		36.30 Kcal/mole
3. Apparent heat of solution of crystalline dye in polyester,[b] ΔH°		7.44 Kcal/mole
4. Apparent heat of dyeing from $\log K \rightarrow 1/T$ (Fig. 11), ΔH_D°		28.33 Kcal/mole
5. $-\Delta H_D^\circ = \Delta H_S^\circ - \Delta H^\circ$		28.86 Kcal/mole

[a] Values in 1 and 2 are taken from earlier publications.[6]
[b] ΔH° calculated from Figure 10.

It is seen from the values given in Table I that the values of ΔH_D° calculated by both methods are almost identical. The data on various heat terms for the process are also given in the same table. No attempt has been made to calculate ΔS_D° and interpret the molecular mechanism when only apparent entropy values are known.[6]

From the foregoing discussion it follows that even after prolonged fixation all the dyestuff from viscose portion cannot be transferred to polyester portion. On soaping the dyed union, it is not possible to remove all the unfixed dye from the viscose portion (Fig. 12); it thus confirms the earlier view that part of the dyestuff diffuses inside the fine structure of viscose fibers.[6] However this stain on the viscose portion, $(D_W^\sigma$, can be easily removed by wetting with hot water and extraction in cold dimethylformamide. The stain on the viscose portion of the union increases and then remains almost constant with increase in fixation time t. The staining property seems to depend on the dyestuff; for example, the staining of the viscose portion is more with dyestuff I than with II. If the stain on the viscose portion could be related to the dyestuff that has entered the fine structure of the
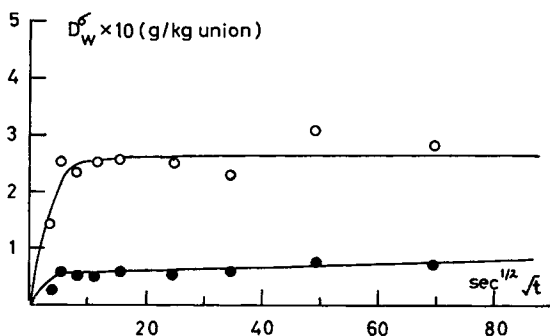

Fig. 12. Relationship between dye remaining on viscose portion, D_W^σ, of union fabric after soaping and the time of fixation at 195°C. Precision Laboratory Press: (O) dye I; (●) dye II. (Concentration of deposited dye I or dye II on union $D_{TV}^\sigma = 7.78$ g/kg union.)

fiber, then the difference observed in the behavior of dyestuffs I and II is understandable in view of their molecular size.

CONCLUSIONS

Using typical examples from the extensive experimental data available, it is shown how the distribution of a disperse dyestuff takes place during different stages of the thermofixation process. It is possible to deduce fairly simple semiempirical rules regarding the phenomenon of thermofixation of polyester–viscose union. However, it is not possible to derive an exact thermodynamic theory to explain the data and describe the molecular mechanisms in such systems.

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