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THE APPLICATION OF THE ETTERS DIFFUSION EQUATION TO THE RATES OF ABSORPTION OF CHROMIUM BY DYED AND UNDYED WOOL

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ABSTRACT

A simple diffusion equation, has been successfully used to monitor the initial fast absorption of chromium by both dyed and undyed wool. The diffusion coefficients (D values), describing the rates of absorption (diffusion) of chromium by (into) wool, show an unusual reversal of normal reaction kinetics for undyed wool where an increase in chroming temperature causes a decrease in the rate of absorption of chromium by the wool. This has been ascribed to the rate of deposition of chromium III in the wool fibre, produced by the reduction of the exhausting chromium VI species. Furthermore, the apparent activation energy (Ea values), necessary for the exhausting chromium VI species to overcome the chromium III barrier, increased with decreasing pH and was independent of acid type. With dyed wool substrates, on the other hand, it was shown that an increase in chroming temperature caused an increase in the rate of absorption of chromium. The apparent activation energy necessary for chromium to be absorbed by dyed wool decreased with decreasing pH and was independent of acid type.

INTRODUCTION

In spite of the obvious importance of understanding the kinetics of the chroming process, a study of the literature has shown that there are a number of controversies which still exist[1]. To date only certain specific aspects of the kinetics of the chroming of wool have been dealt with[2-9], and, because of the diverse nature of the reaction conditions employed by different workers, it is not possible to relate the different results to one another in a meaningful way. However, a generally accepted concept is the fact that the absorption of chromium by wool can be described as having two rates, viz. an initial very fast absorption followed by a slower absorption. For this particular investigation it was decided to monitor the rate of absorption of chromium by wool over the initial period and then describe this absorption in terms of the diffusion coefficients (D) and apparent activation energies (Ea).

After having pursued an exhaustive survey of numerous kinetic (diffusion) equations, surprisingly, the Etters[10] diffusion equation for disperse dyeing systems was considered to best fit the experimental data. Etters has produced a simple diffusion equation from which analytical approximations can

be made with a high level of accuracy. He found, by using curve fitting techniques, that an equation of the form:

$$M_t / M_\infty \quad \left[1 - \exp \left\{ -k (Dt/a^2) \right\}^x \right]^{\frac{1}{y}} \quad \dots\dots\dots(1)$$

or rearranged to give:

$$\left[\left\{ -\ln \left[1 - (M_t / M_\infty)^y \right] \right\} / k \right]^{\frac{1}{x}} = D/a^2 . t$$

reproduces with a high degree of accuracy, the functional relationships expressed by the conventional equations:

where M_t = Amount of material (chromium) on the fibre at the time = t

M_∞ = Amount of material (chromium) on the fibre at the time = ∞

D = Approximate diffusion coefficient (cm^2/s)

a = Value for the average radius of the wool fibres (11×10^{-4} cm).

The parameters k, x and y are purely empirical approximations and are given as:

$$k = \exp \left\{ 1,7824 (1 - E_\infty)^{-0,0713} \right\}$$

$$x = (0,2837 + 0,8133 \sqrt{1 - E_\infty})^2$$

$$y = 2,6081 (1 - E_\infty)^{0,7014}$$

Where E_∞ is the equilibrium bath exhaustion, related to the intrinsic partition of the exhausting material (chromium) between the bath and the wool fabric and

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depending on the liquor ratio as follows:

$$E_\infty = K_\infty / K_\infty \ + \ r$$

Where $K_\infty = C_{f\infty} / C_{b\infty}$ or the relative amount of material (chromium) in the fibre to the amount in the bath at equilibrium.

r = Liquor ratio — taken as 500.

Using the rearranged form of equation (1), a linear relationship can be obtained between

$$\left[\left\{ -\ln \left[1 - (M_t / M_\infty)^y \right] \right\} / k \right]^{\frac{1}{x}}$$ and t. From the slope of the graph the

diffusion coefficient (D) could be determined. Having obtained the diffusion coefficients at four different chroming temperatures, it was possible to determine the apparent activation energies (Ea) for dyed and undyed wool using the Arrhenius equation[11] and the linear relationship between

$-\ln D$ and $\frac{1}{T}$. The equation is given as follows:

$$D = D_o \ e^{-Ea/RT} \quad \dotfill \quad (2)$$

or $\ln D = \ln D_o - Ea/RT$

where	Ea	=	Apparent activation energy (kcal.mole^{-1})
D	=	Diffusion coefficient
Do	=	Pre-exponential factor independent of temperature and related to the entropy changes on activation
R	=	Gas constant (1,98717 cal.deg^{-1}.mole^{-1})
T	=	Absolute temperature (^oK)

EXPERIMENTAL

A. Materials

A plain weave, scoured all wool fabric* (165 g/m²) produced from wool having a mean fibre diameter of 22,7 μm was used throughout this study.

The dye used was a commercial sample of the ®Eriochrome range, namely: Eriochrome Blue S.E. (C.I. Mordant Blue 13).

De-mineralised water was used for the preparation of all solutions and percentages are expressed on the mass of the conditioned wool.

With the exception of the dyes which were commercial products, A.R. quality chemicals were used for the dyeing and chroming studies.

B. Equipment

A Colora Ultra Thermostat water bath was used to control the water temperature ($\pm$ 0,005°C) in the stainless steel canister, containing the Ahiba Turbomat laboratory dyeing flask, for the kinetic studies. (See Figure 1).
    A Varian AA 175 single beam atomic absorption (A.A.) spectrophotometer with an air-acetylene burner was used for the determination of the concentration of total chromium in solution.
    All pH measurements were made using a Corning-Eel Model 7 pH meter, having facilities for making temperature compensations.

C. Method:

    Two circular wool fabric samples (diameter 6,2 cm) sewn together and having a combined weight of 1 gram were wetted out in de-ionised water at 333°K for 15 minutes. Each kinetic run involved a single 1 gram wool sample placed in a stainless steel basket attached to a magnetic stirrer inside the laboratory dyeing flask. This flask (or dyebath) was then inserted into the stainless steel canister which had its temperature controlled by the Ultra Thermostat water bath and was positioned on a magnetic stirrer, set at a constant stirring rate of 600 rev/min. (See Figure 1).
    Subsequently, each wool sample was treated with a 500 ml aqueous solution of either formic, acetic or propionic acid. Furthermore, each acid was administered in 3 different concentrations, viz. 13,1, 26,2 and 30,3 m.moles of concentrated acid in 500 ml de-ionised water. For studies where *undyed* wool fabric was used, the temperature of the dyebath was then set at either 298, 318,

338 or 368° K and an initial constant amount of potassium dichromate (0,5%) added. For studies where *dyed* wool fabric was used, C.I. Mordant Blue 13 (2%) was added to the bath at 333° K and the temperature raised to 368° K over 30 minutes. Satisfactory exhaustion of the dye onto the wool was obtained after a further 45 minutes at 368° K, after which the temperature was set and potassium dichromate (0,5%) added to the original dyebath liquor as above. A liquor:goods ratio of 500:1 was maintained throughout. From the time of the addition of potassium dichromate, the exhaustion of total chromium onto both
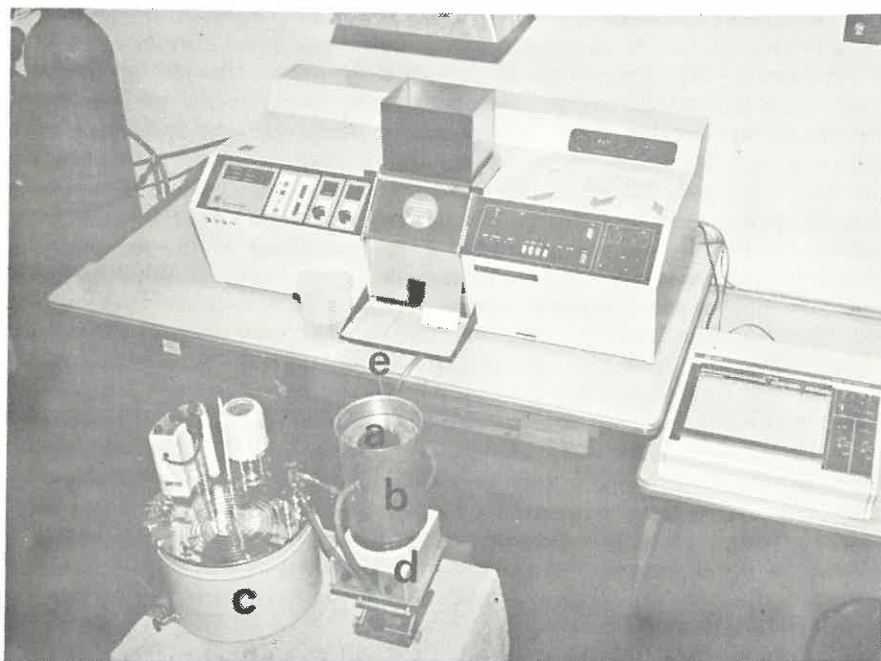

Fig. 1 – The layout of the equipment used for the kinetic studies.

(a) Laboratory dyeing flask

(b) Stainless steel canister

(c) Ultra Thermostat water bath

(d) Magnetic stirrer

(e) Sampling Tube.

dyed and undyed wool was continuously monitored for a period of ten minutes on the A.A. Spectrophotometer. This was done by simply inserting the sampling tube directly into the dyeing flask (see Figure 1). The pH of the liquor in the flask was determined after each kinetic run.

D. Procedures:

To monitor continuously over a period of ten minutes this initial very fast absorption of chromium it was obviously necessary that it should be slowed down some way or other. Previous workers had always used liquor ratios in the region of 50:1 down to 20:1. This, in terms of initial concentration difference between chromium in the liquor and chromium on the wool, affords a powerful driving force for the absorption of chromium by wool, considering the high affinity that chromium has for wool, especially when exhausted from acid dyebaths. It was decided, therefore, to increase the liquor ratio to 500:1, which, even in a well stirred dyebath, allows for a more gradual absorption of chromium, i.e. close approach of the individual chromium containing anions to the surfaces of the wool fibres is less frequent as a result of the high dilution of the solution. A further advantage of the extended liquor ratio was that the chromium concentrations in the dyebath could be continuously monitored on a A.A. spectrophotometer without having to dilute the solutions.

Since a liquor ratio of 500:1 was used, it was found necessary to reduce the dye concentration slightly, from 3% to 2% o.m.f. as this lower concentration gave the complete dye exhaustion which was required for this study. The chromium VI additions (set at 0,5% o.m.f.) created a dyebath concentration of $10 \ \mu g \ Cr/m\ell$. The acids used for the control of dyebath pH, during the exhaustion of dye (dyed wool samples) and of chromium were the organic acids, formic, acetic and propionic acid, each administered in 3 different concentration doses. To complete the study, the rates of exhaustion of chromium onto the dyed and undyed wool samples were monitored at four different pre-set dyebath temperatures, viz. 298, 318, 338 and 368°K. This involved a total of 72 individually monitored reactions.

These continuously monitored chromium exhaustion curves produced on the A.A. spectrophotometer strip chart recorded were corrected for drift, evaluated at 1 minute intervals, normalised and fed into a small computor which was used for the calculations. Figures 2 and 3 are examples of the types of exhaustion curves obtained for dyed and undyed wool, when chromed in the presence of 26,2 m.moles of acetic acid.

RESULTS AND DISCUSSION

The results obtained on undyed wool are introduced first. As already mentioned, the empirically established equation (1) which examines the exhaustion of chromium onto wool over a period of 600 seconds (10 minutes),
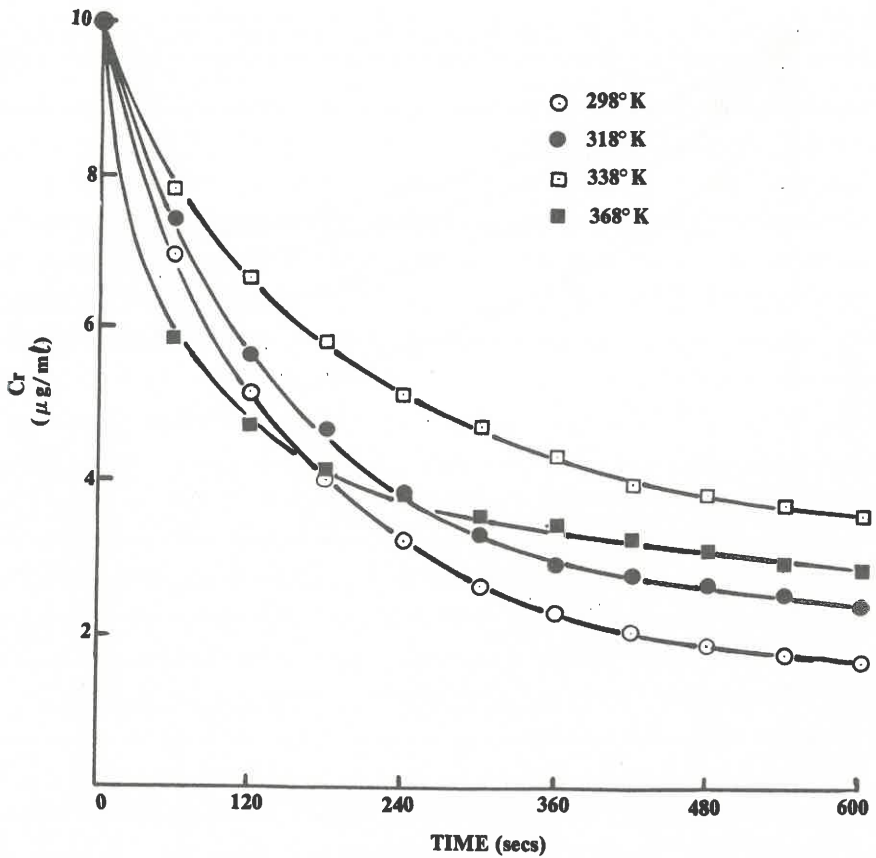
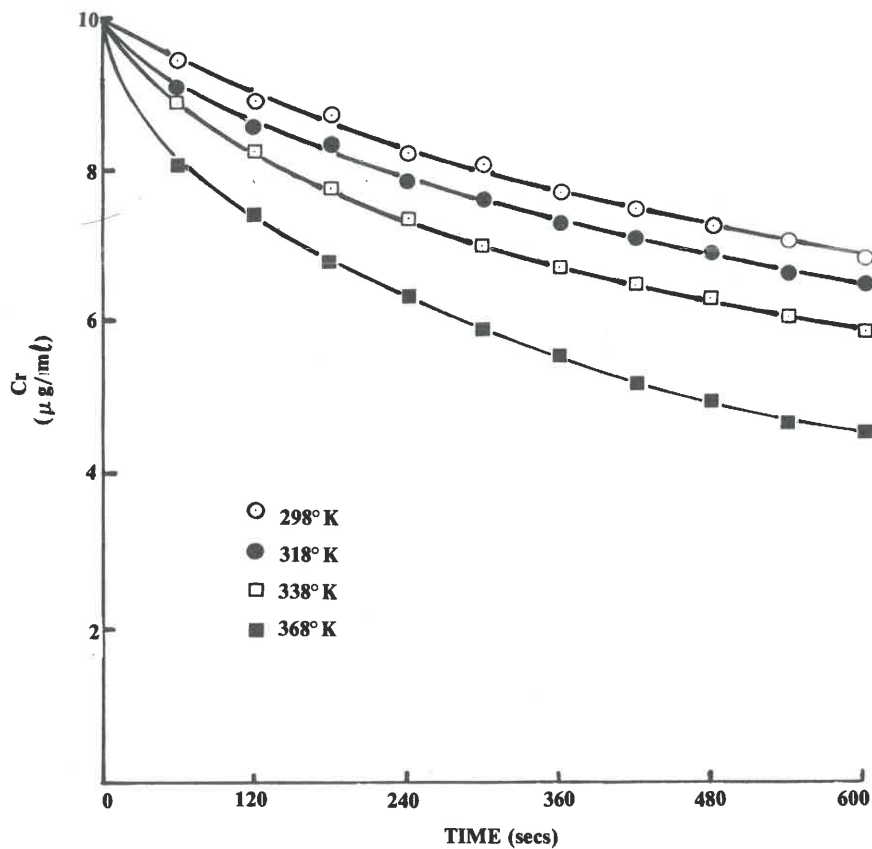Fig. 2 – *The apparent rates of exhaustion of chromium onto undyed wool (26 m.moles acetic acid).*

Fig. 3 – The apparent rates of exhaustion of chromium onto dyed wool (26 m.moles acetic acid)

TABLE I

DIFFUSION COEFFICIENTS, D ($\times 10^{-10}$ cm^2/sec) DETERMINED ACCORDING TO EQUATION (1)

UNDYED WOOL

Temperature (°K)	Formic Acid Conc. (m.moles)			Acetic Acid Conc. (m.moles)			Propionic Acid Conc. (m.moles)		
	39,3	26,2	13,1	39,3	26,2	13,1	39,3	26,2	13,1
298	3,94	4,29	4,34	3,83	4,70	3,69	3,68	6,31	2,83
318	2,66	2,55	3,02	3,46	3,35	3,10	2,64	2,62	2,45
338	1,71	1,83	1,97	2,36	2,13	1,94	1,72	1,90	1,70
368	1,50	1,71	1,88	1,99	2,04	2,08	1,51	2,16	1,93

DYED WOOL

Temperature (°K)	Formic Acid Conc. (m.moles)			Acetic Acid Conc. (m.moles)			Propionic Acid Conc. (m.moles)		
	39,3	26,2	13,1	39,3	26,2	13,1	39,3	26,2	13,1
298	1,26	1,21	1,08	0,40	0,37	0,42	0,56	0,45	0,22
318	1,50	1,74	0,88	0,66	0,56	0,53	0,63	0,99	0,29
338	1,33	1,48	1,18	0,81	0,75	0,54	1,21	0,48	0,36
368	2,87	2,50	2,42	2,14	1,84	1,41	1,45	1,63	1,12

fits the data adequately for undyed wool. Table 1 shows the trends for these diffusion coefficients, determined according to equation (1). It can be seen clearly that an increase in chroming temperature produced a decrease in the diffusion coefficients which appeared to be independent of acid type or concentration in the liquor.

Furthermore, at each set chroming temperature, the effect of acid type and concentration in the liquor on the diffusion coefficients would seem to be rather complex. This aspect is clarified later when discussed in terms of liquor pH. An example of the linear dependence of -ln D against $\frac{1}{T}$ (the Arrhenius equation (2) for the entire temperature range can best be seen in Figure 4 (undyed wool).

In the case of dyed wool, an increase in chroming temperature caused an increase in the magnitude of the diffusion coefficient, irrespective of acid type or concentration in the liquor (see Table I). The magnitude of the diffusion coefficients, at each set chroming temperature for dyed wool, tended to decrease when going from formic to acetic and to propionic acid. There was, furthermore, a general decrease in the diffusion coefficient with decrease in acid concentration for each acid at each set chroming temperature. A plot of -ln D against $\frac{1}{T}$ produced a very good fit for the Arrhenius equation (2). This can also be seen as an example in Figure 4 (dyed wool).

The apparent activation energies, Ea, determined from the Arrhenius equation, or, the linear dependence of the natural logarithm of the diffusion coefficients on the temperature inverse, can be seen in Table II for both dyed and undyed wool. There was a very good correlation between the apparent activation energies and the 'averaged' pH values of the liquor as can be seen in Table II and also in Figure 5. After each experiment the pH of the liquor was measured. Although there was very little difference between the start and end (after 10 minutes) pH values of the solutions of experiments carried out at the different temperatures, there were significant differences in the pH of the liquors for the varying acid concentrations and acid types, as was to be expected. Furthermore, there were significant differences between the results obtained on dyed and undyed wool. This can be seen in Table II where an 'averaged' pH has been determined (over the 0-10 minute period) for the entire temperature range. Steinhardt et al [12] also found that temperature had a negligible effect on the equilibrium between weak acids and wool.

When examining the kinetics of the chroming process it is important to note the state of the wool fibre before addition of chromium. The wool, having been wetted out properly with water, is first treated with pre-determined amounts of acid. Although the molar quantities of acid used were the same for
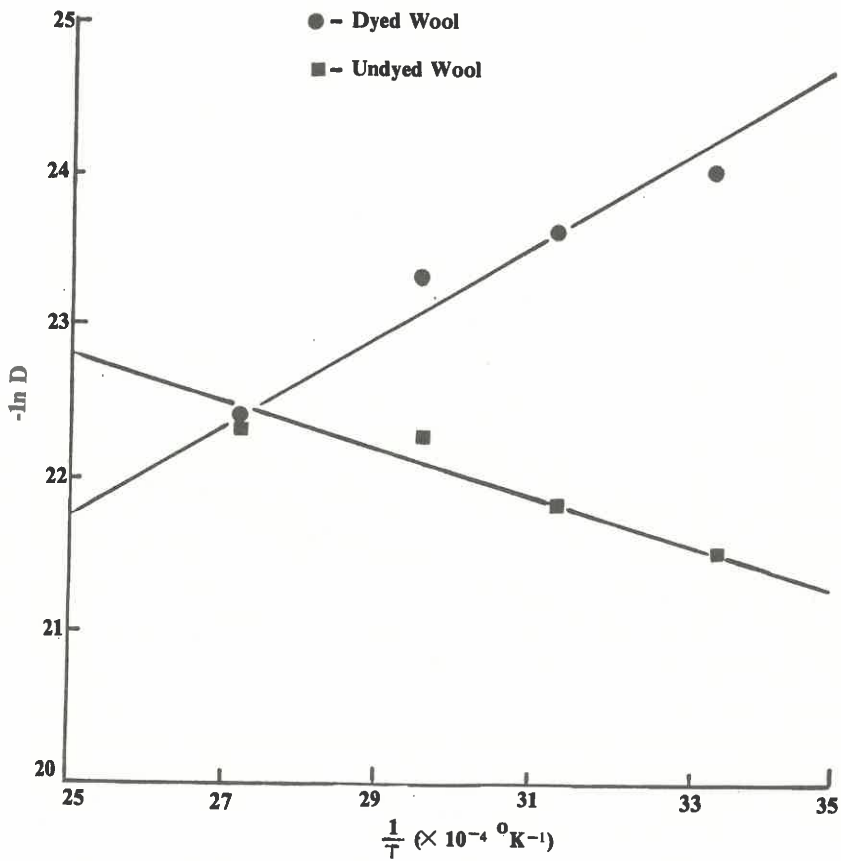
Fig. 4 – *The temperature dependence of the diffusion coefficients.*
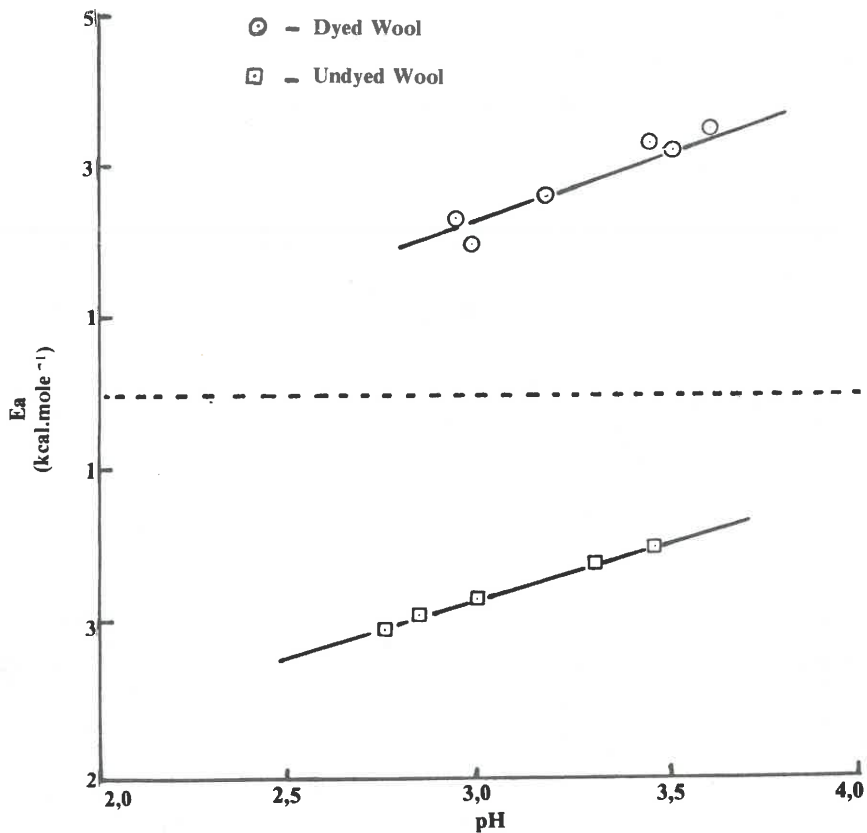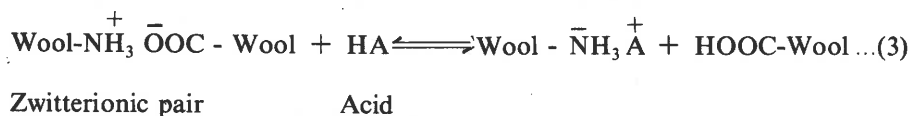*(26,2 m.moles acetic acid)*

Fig. 5 – The apparent activation energies expressed as a function of the average liquor pH.

TABLE II

THE APPARENT ACTIVATION ENERGIES Ea (kcal.mole $^{-1}$) DETERMINED FOR DYED AND UNDYED WOOL AND THEIR AVERAGED pH VALUES

UNDYED WOOL

	Formic Acid Conc. (m.moles)			Acetic Acid Conc. (m.moles)			Propionic Acid Conc. (m.moles)		
	39,3	26,2	13,1	39,3	26,2	13,1	39,3	26,2	13,1
Averaged pH	2,75	2,80	2,99	3,35	3,33	3,46	3,31	3,40	3,55
Ea	-3,1	-2,9	-2,7	-2,2	-2,7	-2,0	-2,9	-3,2	-1,1

DYED WOOL

	Formic Acid Conc. (m.moles)			Acetic Acid Conc. (m.moles)			Propionic Acid Conc. (m.moles)		
	39,3	26,2	13,1	39,3	26,2	13,1	39,3	26,2	13,1
Averaged pH	2,94	2,98	3,18	3,39	3,49	3,61	3,45	3,51	3,72
Ea	2,3	2,0	2,6	4,9	4,8	3,5	3,3	3,2	4,8

all three acids at the three different concentration levels, the amount of hydrogen ions H^+) diffusing into the fibre, according to equation 3 below

$$\text{Wool-}\overset{+}{N}H_3\ \overset{-}{O}OC\text{ - Wool} + HA \Longleftrightarrow \text{Wool - }\overset{-}{N}H_3\overset{+}{A} + HOOC\text{-Wool} \dots(3)$$

Zwitterionic pair   Acid

is determined primarily by the ionization constant for the three acids in water at the various temperatures. For example, at 323° K, the ionization constants are as follows[13]:

Formic acid   -   Ka   - $1{,}650 \times 10^{-4}$

Acetic acid   -   Ka   = $1{,}633 \times 10^{-5}$

Propionic acid   -   Ka   = $1{,}229 \times 10^{-5}$

       It is therefore conceivable that 39,3 m.moles of formic acid in 500 mℓ of solution would produce more hydrogen ions in the solution and would therefore be able to supply more hydrogen ions to the wool [back titration of the carboxyl groups according to equation (3)] than 39,3 m.moles of acetic acid, which in turn would produce more hydrogen ions than 39,3 m.moles of propionic acid. Therefore the degree of back titration of the carboxyl groups in the wool by the hydrogen ions is of prime importance, being in the order — formic $>$ acetic $>$ propionic acid, and, logically, also decreased when the acid concentration decreases from 39,3 to 13,1 m.moles of acid in 500 mℓ of solution. Also of

importance, is the degree of association of the acid anions (A^-) with the

protonated amino groups ($-NH_3^+$) in wool, which could depend on their relative affinities for these amino groups or their relative molecular size in the fibres, viz. propionic $>$ acetic $>$ formic acid anions.

       Returning to the chroming process, having treated the wool with predetermined amounts of acid and allowed it to reach equilibrium with the acid, the dye may now be introduced. The introduction of the dye anions (dyed wool)

to the dyebath, merely displaces some of the acid anions (A^-) by virtue of their greater affinity for the protonated amino groups, c.f. equation (3). The displaced acid anions eventually find their way back into the dyebath. Provided that the dye concentration on the fibre is kept constant for all the acids, the only effect of varying the acid concentration would be a variation in the number of protonated amino groups which are associated with acid anions. Obviously in the case of

undyed wool, the majority of the amino groups would still be associated with acid anions, compared to the dyed wool where a considerable number of the acid anions have been displaced by dye anions.

The anionic chromium VI was added to the acid bath containing dyed or undyed wool. The undyed wool/chromium VI system will be examined first. The relatively small, highly charged chromium anions rapidly diffused from the liquor onto the surface of the wool fibres, easily displacing any acid anions associated with the protonated amino groups on or near to the surface by virtue of their far higher affinity. This was followed by a more gradual diffusion of these anions deeper into the fibre, the speed of which is controlled by —

(i) Steric hindrances, due to the highly complex orientation of fibre molecular chains (helices).

(ii) Liquor pH. The fact that once present on or in the fibre, these Cr VI anions reduce the number of protonated amino groups available by their close association, and in so doing create a less favourable situation for those anions following. Obviously acid concentration and acid strength (Ka value) would play a role here in determining the number of available protonated amino groups. Furthermore, it is known that a decrease in the liquor pH value increases the rate of reduction of Cr VI to Cr III on wool[5].

(iii) Temperature. The rate of reduction of chromium VI to chromium III by certain groups in the wool, e.g. cystine, methionine and tyrosine[14], seems to be also temperature dependent. Undoubtedly Cr III forms rapidly in the fibre especially at high temperatures; in fact, almost as fast as Cr VI is being exhausted, as was shown by the work of Rattee[15]. It is logical, therefore, to assume that a lowering of the dyebath temperature would likewise reduce the rate of formation of Cr III. At room temperature (298°)k) the reduction would be extremely slow, and it has in fact been shown to be negligible[16] in the presence of non-reducing acids.

This study has shown (Figure 2 — Table I) that the rates of exhaustion of chromium onto, and diffusion into undyed wool in terms of the diffusion coefficients becomes progressively slower as the temperature was increased. It is envisaged that the formation of Cr III in the fibre retards the progress of the incoming Cr VI, either by cross-linking the amino and carboxyl groups according to mechanisms referred to previously[5], or by absorbing large amounts of hydrogen ions according to the classical reduction reaction as follows[17]:

$$Cr_2O^=_7 \; + \; 14H^+ + \; 6e' \; \longrightarrow \; 2Cr^{+3} \; + \; 7H_2O \; \dots\dots\dots\dots(4)$$

In this latter process, the formation of Cr III changes the internal pH of the fibre system while the Cr III is being bound to the carboxyl groups as

postulated by Hartley[14]. Because of the long liquor ratios used (500:1) for these studies, very little change could be detected in the pH values of the liquors during the chroming process. The reduction reaction (Equation 4) requires hydrogen ions (H^+), which can be obtained either from the internal solution, i.e. those produced by the acid, or alternatively from water, leaving hydroxyl ions[18] in the internal solution, once again increasing the negative charge inside the fibre, which is not conducive to Cr VI exhaustion.

It can be concluded, therefore, that the retardation of the Cr uptake by wool with increase in temperature, was mainly due to the formation of Cr III. This reaction can be compared with the analogous situation which arises during the exhaustion of acid permanganate onto wool. Alexander *et al*[19] have shown that permanganate (MnO_4^-) is rapidly exhausted onto wool, where it attacks the disulphide bond (cystine) and tyrosine with the subsequent deposition of manganese dioxide (MnO_2) in the fibre. It was found that increasing quantities of MnO_2 in the fibre retarded the rate of exhaustion of MnO_4^-. When the MnO_2 deposits were removed from the fibre, however, the rate of exhaustion of MnO_4^- once again increased.

Further support for this concept has come from Dobozy[5], who is of the opinion that the reduction of Cr VI to Cr III has an induction period, but once it has started, it proceeds like a chain reaction, which rapidly oxidises the disulphide bonds in the wool. This is not an entirely new concept, since Gal and Guczi[20] have shown that the oxidation of cystine can proceed through a chain reaction. According to Dobozy[5], and this author, therefore, the rate of exhaustion of Cr VI onto the wool is initially regulated by diffusion but after the accumulation of Cr III on the fibre has started, the exhaustion of Cr VI is not determined by diffusion, but by the amount of Cr III formed.

It is evident from Table I that for undyed wool, acid type and concentration also play a role in determining the diffusion coefficients (D). In general, an increase in acid concentration should increase the 'D' values. However, in the case of formic acid, an increase in concentrations causes a general decrease in the 'D' values. The lowest averaged liquor pH values are recorded with formic acid and it is likely that formic acid acts as a catalyst for the reduction of Cr VI to Cr III on wool under these conditions (see Table II). It is well known that concurrent with a decrease in the pH of the liquor, the chromium oxidation-reduction potential also decreases, thereby accellerating the reduction of Cr VI to Cr III[5]. In other words, the retarding effect due to the formation of Cr III in the wool overshadows the effect of an increased number of protonated amino sites. Acetic acid, on the other hand, producing higher liquor pH values and not being able to so strongly catalise the Cr VI reduction, shows a general increase in 'D' values with increase in concentration up to 338°K, whereafter (at 368°K) no trend was noticed (or the trend was, if anything, reversed). Therefore, with acetic acid the 'D' values were more delicately

controlled by the balance between availability of sites for binding Cr VI and the retarding effect of the presence of the Cr iII, with the formation of Cr III being mainly temperature dependent and perhaps to a small extent, pH dependent. The weakest of the acids, namely propionic acid gave varying 'D' values when increasing the acid concentration but would seem to be in keeping with the general trends that were found for acetic acid and the same arguments may therefore be applied.

Finally, for undyed wool, it was found that these 'D' values, which decreased with increasing temperature when fitted to the Arrhenius equation (2), were linear, but obviously produced negative (Ea) activation energy values (see Figure 4 for example, and Table II). The values are in fact an indirect measure of the apparent energy needed by the exhausting chromium VI species to overcome the chromium III barrier. It is clear in Table II that for undyed wool, the 'Ea' values in absolute terms generally decrease with decreasing acid concentration and decreasing acid strength (i.e. from the left to the right). This indicates a decreasing energy requirement in this direction and conforms with the arguments put forward for the chroming of undyed wool. In fact, if acid type is disregarded and acid strength or concentration is taken into account in terms of final liquor pH (Table II), it is found that the apparent activation energy (Ea) is linear and increases with decreasing pH (see 'undyed wool', Figure 5).

The case of the dyed wool will now be examined in the light of what has been proposed for undyed wool. It is clear that in the case of dyed wool the diffusion coefficients (D) generally increase with increasing temperature, which conforms with normal thermodynamic principles. These trends may be seen in Table I. Furthermore, there is a general decrease in the 'D' values with decreasing acid strength and acid concentration (i.e. increasing pH). These trends may be ascribed to the following factors:

(i) Enhanced steric hindrances, due to the mere presence of a rather bulky dye molecule in the fibre, as well as the contribution from the orientation of the fibre molecular chains or helices.

(ii) Liquor pH (see Table II). The recorded liquor pH values were higher for dyed wool than undyed wool regardless of acid type or concentration. A fairly large proportion of the hydrogen ion concentration was more than likely associated with the dye. This was not conducive to the reduction of Cr VI to Cr III, nor does it auger well for the availability of hydrogen ions (H^+) which were necessary for the production of protonated amino groups as well as for the reduction reaction. Furthermore, the dye carried a negative charge and has occupied many of the protonated amino sites in the fibre. The negatively charged dye molecule would repel the Cr VI anion by repulsion and because of the affinity of the dye for the protonated sites, it cannot be easily displaced

by an energetically excited Cr VI anion. The Cr VI anion therefore has to diffuse or migrate to some alternate sites which may not contain acid anions (A $^-$) which are displaceable.

(iii) Because of (i) and (ii) above there would be considerably less Cr VI on the dyed wool than on the undyed samples at any time during the initial stages of chroming. Certainly much more energy, (in terms of temperature) would be required to promote the absorption of chromium by the wool, in the former case. It follows therefore, that, for the above reasons and because there was less Cr VI present in the fibre, less Cr III may be formed. This should not be confused with the rate at which Cr III is formed in dyed wool, which may in fact be enhanced by the reducing capabilities of the dye in certain cases. In any case, it is felt that the Cr III is complexed by the dye molecules as fast as it is formed in the dyed wool. Once complexed to the dye, the Cr III is apparently no longer able to cross-link or bind the fibre in any way and so inhibit the diffusion of Cr VI as pronouncedly as with undyed wool. It is felt that complexformation merely promotes the hindrances created by (i) and (ii). Therefore, temperature becomes the driving force which promotes Cr VI diffusion into the fibre, as well as reduction to chromium III and complexformation with the dye molecules.

As indicated before, this can be seen in Table I where an increase in temperature generally enhanced the 'D' values for dyed wool, while a decrease in acid strength and acid concentration generally decreased 'D' values. The 'D' values obtained for dyed wool also produced good linear fits when applied to the Arrhenius equation (2). In this case the apparent activation energies (Ea) were positive and generally increase with decreasing acid strength and acid concentration (see Table II). This is in accordance with the concept that more energy is required to promote exhaustion and diffusion of Cr VI into the wool, the weaker the acid strength and lower the concentration (thus producing less $-NH_3^+$ groups). In fact, if the final liquor pH of the dyed wool samples is considered (Table II), it seems that the apparent activation energy (Ea), decreased linearly with decrasing pH (see 'dyed wool', Figure 5). However, if one looks at the three different acids separately, this is not so obvious.

It is interesting to compare the 'Ea' obtained with dyed and undyed wool. For the same reaction conditions, the 'average' difference in energy is approximately 6 kcal.mole $^{-1}$, and it was apparently independent of acid type, concentration or liquor pH (see, for example, the energy difference between the two parallel lines for dyed and undyed wool in Figure 5). This difference between the 'Ea' values obtained with dyed and undyed wool could be attributed to the energy requirement necessary for the Cr III-dye complex formation and fixation. Coates et al [21] have shown that the energy necessary for the formation

of the 1:1 chromium III-dye complex with cystine and glycine is of the order of 4-6 kcal.mole^{-1}, which is of the same order of magnitude as the values obtained in this investigation.

SUMMARY AND CONCLUSION

Briefly, it may be stated that, for undyed wool, an increase in chroming temperature causes a decrease in the rate of absorption of chromium by wool. This unusual reversal of normal reaction kinetics may be ascribed to the rate of deposition of Cr III in the wool fibre, produced by the reduction of the exhausting Cr VI species. The presence of an increasing amount of Cr III in the wool retards further uptake of Cr VI. Furthermore, it has been shown that the reduction reaction (Cr VI — Cr III) may be enhanced not only by increasing the chromimg temperature, but also by lowering the pH of the system. In accordance with the above theory, it was shown that the apparent activation energy needed by the exhausting Cr VI species to overcome the Cr III barrier increased with decreasing pH and was independent of acid type.

In the dyed wool species, however, an increase in chroming temperature caused an increase in the rate of absorption of chromium. Because of the large number of protonated amino sites in the wool occupied by the dye and its rather bulky size it retards the uptake of chromium. The Cr III, produced by the reduction of Cr VI, is complexed with the dye and seems to be no longer able to retard the progress of the incoming Cr VI anion (as in the case of undyed wool). Temperature, therefore, becomes the driving force, coupled with a decrease in the pH of the system (creating alternate protonated amino sites) for the absorption of chromium by dyed wool. Lastly, the apparent activation energy necessary for chromium to be absorbed by dyed wool was shown to decrease with decreasing pH, once again independent of acid type and in accordance with the above theory.

In summarising this study, it is clear that the diffusion equation (1) producing diffusion coefficients ('D' values) and the Arrhenius equation (2), producing apparent activation energies ('Ea' values), adequately describes the effect of the presence of various organic acids in the liquor (controlling the pH), the presence of dye on the wool as well as the effect of chroming temperature on the rates of absorption of chromium by wool.

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THE USE OF PROPRIETARY NAMES

The names of proprietary products where they appear in this report are

mentioned for information only. This does not imply that SAWTRI recommends them to the exclusion of other similar products.

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