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# The Effect of Amino Acids on the Adsorption of Direct Red on Cellulose Fibres

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Equilibrium adsorption isotherms and rates of dyeing for Direct Red on cotton fibres pretreated with solutions of Valine, Threonine, Proline and Histidine in aqueous acetic acid were measured. Amino acid treatment increased the rate of dyeing with Direct Red and improved the wet fastness properties of the dyed cotton. At lower concentrations of amino acids, the order of exhaustion value was Threonine > Valine > Proline > Histidine whereas at higher concentrations, the order changed as Threonine > Proline > Valine > Histidine.

***Key words:*** Direct red dye, Amino acids, Cellulose fibre, Dyeing rate.

## Introduction

Cellulose fibre is composed of very long and flexible molecules. They can be described as polymeric in nature,consisting essentially of many hundreds or even thousands of identical chemical repeat units joined end to end to form polymer chains, but also held together by a variety of inter-chain forces and bonds. Cotton consists of D-glucose units, each containing three hydroxyl groups that contribute to the attachment of direct dyes to cellulosic fibres. Studies on scale models have shown that the structures of dyes that are substantive to cellulose and the cellulose surface itself are similar to each other (Vickerstaff 1954).

Most fibres and dyes contain groups that can take part in this type of intermolecular combinations. The importance of hydrogen bonds in dyeing of certain fibres is evident. Hydrogen bond should form between these hydroxyl groups and azo, amino, hydroxy or amide groups in the dye molecule (Vickerstaff 1954; Allen 1971).

It is believed that direct dye molecules enter cavities in the structure of cellulose and become attached to two or more hydrogen bonds. The observed association between substantivity and tendency of the dye to aggregate in solution may signify that the forces causing aggregation are of the same nature as those responsible for the attraction between fibre and dye, namely Vander Waals forces. For maximum substantivity, not only should direct dye molecules be linear, but their benzene nuclei should also lie in the same plane (Hodgson 1933).

The electrons of the conjugated system of the dye molecule contribute to substantivity since it is thought that the extended electron system is capable of forming an intermediate layer between the cellulose and the water molecules, since interaction can occur between delocalized electrons and the hydroxyl groups on each side.

The process of dyeing cotton with direct dyes is reversible in every case, and all the adsorbed dye can be removed by prolonged washing with water. Despite much research, the direct dyeing of cellulosic fibres is incompletely understood (Allen 1971).

Riad *et al.* (1991) reported that the presence of small amount of organophosphonate sequestrant in the dyeing of cotton with direct dye brings about more rapid dyeing and is accompanied by better fixation of the dye to the cotton fibres. Phosphonates inhibit crystallization and are used to control scale formation in boiler and cooling tower waters (Leeden *et al.* 1982; Rizkalla 1983; Weijnen *et al.* 1983; Hamza & Nancollas 1985 a&b).

Certain amino acids, found as urinary constituents, are capable of preventing formation of calculi in biological systems. Histidine, tryptophane and other amino acids of relative low molecular masses were found to suppress growth and formation of calcium oxalate/hydrates in a manner similar to that of phosphonates (Brecevic & Krali 1986). These facts justified study of the influence of amino acids on the direct dyeing of cotton.

A series of dyeing experiments were, therefore, carried out in which Direct Red was applied to unmercerised cotton fibres, either alone or in the presence of traces of Valine, Threonine, Proline and Histidine. The exhaustion of the dyebath in each case was determined spectrophotometrically.

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## Experimental

*Dyeing of Cotton.* Direct Red (0.02 g), sodium chloride (1 g) and six drops of glacial acetic acid were added to 100 ml distilled water. A test protion of the dyebath (1 ml) was withdrawn and introduced into a 10 ml measuring flask which was filled to the mark with distilled water. The absorption of the solution over the range 450-550 nm was recorded. The dye bath was boiled under reflux and 1 g unmercerized cotton was introduced into it, the time of addition representing the zero time of dyeing. Continuous boiling of the dyebath ensured uniform circulation of the dye liquor around the fibres. After minute intervals, about 1 ml of the dye bath was withdrawn, left to cool at room temperature and then exactly 1 ml of it was introduced in a 10 ml measuring flask, which was filled to the mark with distilled water. The concentration of the dye in the solution was determined spectrophotometrically.

For dyeing with amino acids, cotton (1g) was first immersed for 24 h at room temperature in a solution containing the amino acid (1.0, 1.3, 1.6, 1.9, 2.2 and 2.5 mg) in 100 ml distilled water acidified with six drops of glacial acetic acid (pH of solution 4.0) to attain equilibrium adsorption. Cotton was removed from the amino acid solution, well pressed then dyed with the direct dye as given above.

*Desorption Test on Dyed Cotton.* Two samples of cotton fibres (1 g each) were dyed with 2% Direct Red, one in the absence and the other in the presence of Proline (20 mg). Before carrying out the desorption tests, both samples were boiled under reflux in the dyebath for exactly 1h, removed immediately from the dyebath, pressed well and rinsed with 100 ml distilled water for 1 minute, pressed again and finally boiled under reflux in 100 ml distilled water. After time intervals of one minute, 1 ml samples of the washing solution were withdrawn and their dye content determined spectrophotometrically.

The above technique was repeated. After rinsing in distilled water, each dyed sample was immersed in 100 ml distilled water for 1 minute then each was placed in a beaker containing 100 ml 2% sodium carbonate solution, which was continuously stirred. The concentration of the dye stripped out in the washing solution was determined as described above.

## Results and Discussion

The structural formula of Direct Red is shown in Fig.1. It possesses an absorption maxima in the visible region of the spectrum at 520 nm. In order to study the effect of amino acids on the rate of cotton dyeing with direct dye, the exhaustion

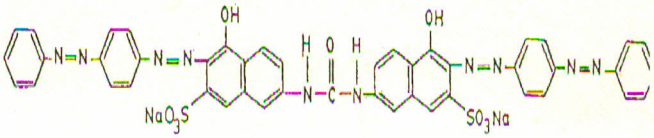

Fig. 1. Structure of Direct Red.

rates of dyebaths containing Direct Red and cotton were determined in the absence and in the presence of Valine, Threonine, Proline and Histidine (Fig. 2) were determined.

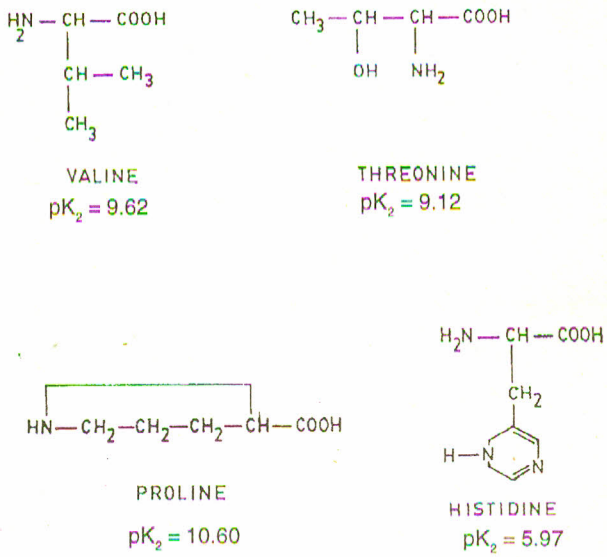


Fig. 2. Structures of amino acids.

Exhaustion rates in the presence of the amino acids were found to be greater than the corresponding rate in their absence (Table 1). The increased uptake of the direct dye may be attributed to the protonation of the amino acids, which can get readily attached by hydrogen bonding to the hydroxyl groups in cellulose. During the dyeing process, the dye anions, each possessing two negatively charged sulphonate groups, were attracted by the positive charge of the protonated amino acid, which was already adsorbed on the surface of the cotton. The results in Table 1 show that an amino acid concentration of approx. 1.0 mg had the following order of decreasing effect on dye exhaustion; Threonine>Valine> Proline>Histidine.

At smaller or higher concentrations, this order of activity changes. The relative effectiveness of the amino acids at the 2.0mg concentration level show the equilibrium as follows:

A shift in the above equilibrium to the left hand side means more attraction between the negatively charged dye anions and the protonated amino acid. If the equilibrium shifted to the

**Table 1**
Exhaustion of direct red dye baths containing 1g cotton at reflux temperatures

| Time (min) | Exhaustion (%) at different amounts of amino acids | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 mg | 1.0 mg | 1.3 mg | 1.6 mg | 1.9 mg | 2.2 mg | 2.5 mg |
| Valine | | | | | | | |
| 10 | 18.00 | 27.68 | 31.26 | 29.48 | 27.30 | 26.87 | 26.36 |
| 20 | 31.00 | 41.01 | 44.50 | 42.89 | 40.84 | 40.26 | 39.70 |
| 30 | 42.00 | 52.08 | 55.48 | 53.60 | 51.74 | 51.32 | 50.78 |
| 45 | 50.50 | 60.74 | 63.52 | 68.95 | 60.51 | 59.58 | 59.18 |
| 60 | 56.00 | 65.88 | 68.94 | 67.42 | 65.56 | 65.16 | 64.71 |
| 90 | 61.30 | 71.57 | 74.48 | 73.75 | 70.40 | 70.09 | 70.41 |
| Threonine | | | | | | | |
| 10 | 18.00 | 36.63 | 33.76 | 30.05 | 28.93 | 28.25 | 28.64 |
| 20 | 31.00 | 50.18 | 47.42 | 43.54 | 42.30 | 41.78 | 41.00 |
| 30 | 42.00 | 59.57 | 57.67 | 54.08 | 53.15 | 52.35 | 52.00 |
| 45 | 50.50 | 67.27 | 65.50 | 62.57 | 61.50 | 60.81 | 60.40 |
| 60 | 56.00 | 72.92 | 70.19 | 67.00 | 66.23 | 65.46 | 64.97 |
| 90 | 61.30 | 77.76 | 75.90 | 72.85 | 72.05 | 70.83 | 70.50 |
| Proline | | | | | | | |
| 10 | 18.00 | 28.00 | 30.30 | 32.20 | 34.30 | 35.10 | 37.10 |
| 20 | 31.00 | 41.36 | 46.00 | 46.61 | 47.74 | 42.50 | 40.54 |
| 30 | 42.00 | 52.05 | 56.46 | 57.46 | 58.11 | 53.60 | 51.60 |
| 45 | 50.50 | 60.54 | 63.87 | 64.50 | 65.70 | 61.75 | 60.36 |
| 60 | 56.00 | 66.16 | 69.33 | 70.10 | 71.17 | 67.13 | 65.46 |
| 90 | 61.30 | 71.09 | 73.98 | 74.87 | 75.52 | 70.82 | 70.51 |
| Histidine | | | | | | | |
| 10 | 18.00 | 25.80 | 24.94 | 23.94 | 24.35 | 24.56 | 25.32 |
| 20 | 31.00 | 39.41 | 38.41 | 37.33 | 37.76 | 38.04 | 38.70 |
| 30 | 42.00 | 49.52 | 49.43 | 48.30 | 48.74 | 53.16 | 49.78 |
| 45 | 50.50 | 58.75 | 57.77 | 57.18 | 57.18 | 57.47 | 58.29 |
| 60 | 56.00 | 64.64 | 63.33 | 62.78 | 62.78 | 62.98 | 63.71 |
| 90 | 61.30 | 69.36 | 68.40 | 67.85 | 67.85 | 68.14 | 69.71 |

right hand side, repulsion would take place between the dye anions and the zwitterionic amino acid.

At higher concentrations (more than 2.0 mg) the order changed as Threonine > Proline > Valine > Histidine. The equilibrium shifted to the right owing to zwitterionic association. Hence less of the protonated amino acid was adsorbed by the cotton, causing a decrease in dye uptake as shown in Table 1. Since the degree of this association changed from one amino acid to another, their relative order of activity, when using smaller or larger concentrations of these acids, differed from that recorded (Table 2). This changing order of activity was due to different degrees of zwitterionic association depending on amino acid structure.

The exhaustion data (Table 1) can be interpreted in terms of Langmuir isotherm.

$$\frac{R_o}{R_o - R_t} = \frac{1}{KC}$$

**Table 2**
Order of exhaustion values for different amino acids

| Amino acid (mg) | Order of exhaustion values |
|---|---|
| 1.3 | Threonine > Valine > Proline > Histidine |
| 1.6 | Proline > Valine > Threonine > Histidine |
| 2.2 | Threonine > Proline > Valine > Histidine |

**Table 3**

Adsorption of dye and amino acid by cotton fibres

| Amino acid | 1/C | $R_o / R_o - R_t$ after 10 min | 20 min | 30 min | 45 min | 60 min | 90 min |
|---|---|---|---|---|---|---|---|
| Valine | 1000 | 8.47 | 6.18 | 7.14 | 8.80 | 9.24 | 9.80 |
| | 769 | 6.87 | 5.10 | 5.80 | 7.01 | 7.45 | 7.90 |
| | 625 | 5.75 | 4.30 | 5.00 | 5.95 | 6.22 | 6.60 |
| | 526 | 4.83 | 3.80 | 4.32 | 5.20 | 5.45 | 5.70 |
| | 454 | 4.45 | 3.40 | 3.85 | 4.60 | 4.80 | 5.05 |
| | 400 | 4.03 | 3.15 | 3.50 | 4.25 | 4.40 | 4.60 |
| Threonine | 1000 | 4.40 | 5.20 | 6.80 | 7.50 | 8.00 | 8.50 |
| | 769 | 3.60 | 4.20 | 5.50 | 6.10 | 6.40 | 6.90 |
| | 625 | 3.30 | 3.70 | 4.80 | 5.20 | 5.60 | 5.80 |
| | 526 | 2.95 | 3.30 | 4.10 | 4.50 | 4.80 | 5.00 |
| | 454 | 2.60 | 3.10 | 4.00 | 4.30 | 4.60 | 4.90 |
| | 400 | 2.35 | 2.65 | 3.35 | 3.60 | 3.85 | 4.05 |
| Proline | 1000 | 8.00 | 5.89 | 5.45 | 5.20 | 7.33 | 8.81 |
| | 769 | 6.66 | 4.60 | 4.42 | 4.12 | 6.00 | 7.23 |
| | 625 | 5.77 | 4.01 | 3.75 | 3.60 | 5.00 | 6.04 |
| | 526 | 4.88 | 3.70 | 3.45 | 3.25 | 4.40 | 5.02 |
| | 454 | 4.33 | 3.30 | 3.12 | 2.90 | 3.95 | 4.65 |
| | 400 | 3.95 | 3.05 | 2.85 | 2.72 | 3.58 | 4.20 |
| Histidine | 1000 | 10.50 | 11.80 | 13.80 | 12.90 | 12.50 | 11.20 |
| | 769 | 8.20 | 9.30 | 10.90 | 10.20 | 9.80 | 8.95 |
| | 625 | 6.80 | 7.80 | 9.20 | 8.60 | 8.10 | 7.45 |
| | 526 | 6.00 | 6.80 | 7.85 | 7.40 | 7.10 | 6.35 |
| | 454 | 5.20 | 6.00 | 6.90 | 6.50 | 6.30 | 5.70 |
| | 400 | 4.80 | 5.45 | 6.30 | 5.90 | 5.65 | 5.10 |

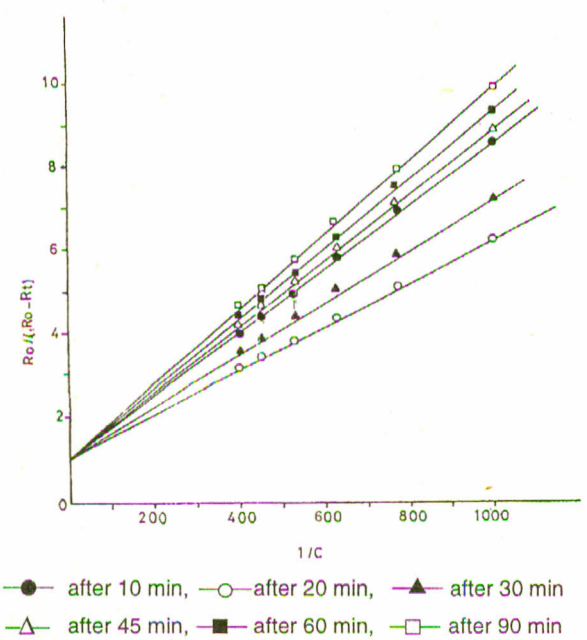


Fig. 3. Adsorption isotherms using different concentrations of Valine.

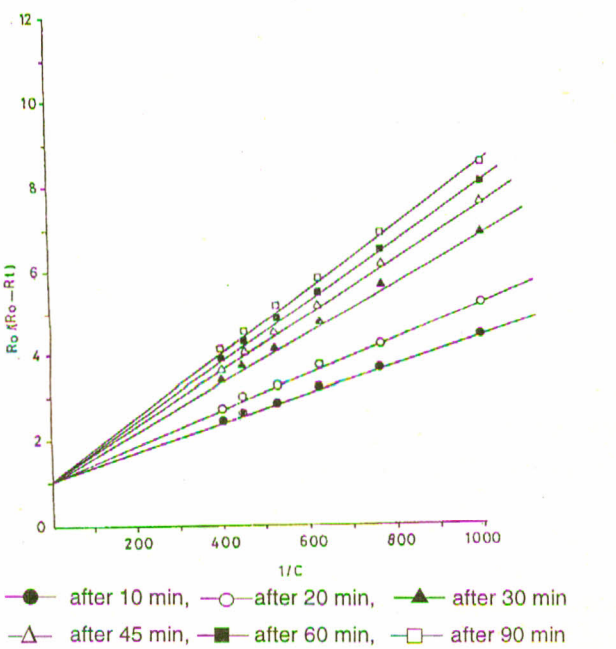


Fig. 4. Adsorption isotherms using different concentrations of Threonine.

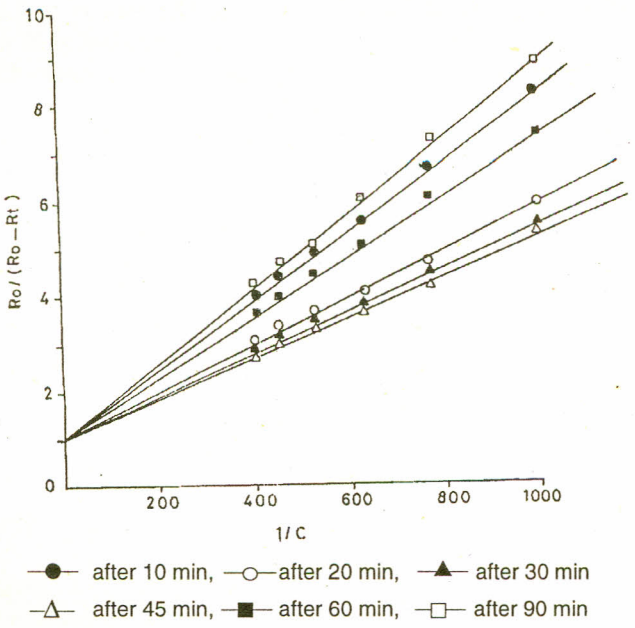


Fig. 5. Adsorption isotherms using different concentrations of proline.

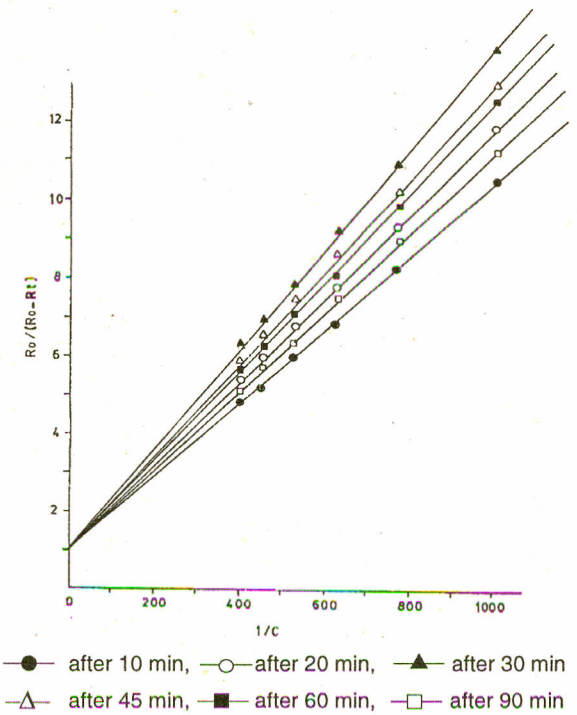


Fig. 6. Adsorption isotherms using different concentrations of histidine.

where

$R_t$ = 100 - exhaustion % in presence of a known weight of the amino acid after a certain period of time.

$R_o$ = 100 - exhaustion % in absence of the amino acid.

K = adsorption coefficient,

C = concentration of amino acid.

The values of 1/C and $R_o/(R_o - R_t)$ at different times using different concentrations of amino acids are given in Table 3. These values are plotted and the adsorption isotherms are given in (Fig. 3-6). These results confirm that dye adsorption takes place on specific sites. The protonated amino acid forms a monomolecular layer on the surface of the cellulose and some amino acid remains in the dyebath, forming a complex with dye anions and decreasing the dyeing rate.

As the dye anions are bonded to the protonated amino acid molecules adsorbed on cotton, this phenomenon results in better wet-fastness properties than in case where no amino acid is present. The results of desorption tests carried out on 1g cotton dyed with 2% direct dye in the presence of amino acid are given in Table 4.

**Table 4**

Amount of dye stripped off 1g cotton fibre dyed with 2% direct red in absence and presence of 20 mg Proline

| | Amount of dye removed (%) | | | |
|---|---|---|---|---|
| | Distilled water at reflux temperature | | 2% Sodium Carbonate solution at room temp. | |
| Time (min) | Proline absent | Proline present | Proline absent | Proline present |
| 10 | 18.1 | 14.0 | 2.5 | 0.9 |
| 20 | 38.1 | 34.3 | 6.8 | 2.5 |
| 30 | 44.3 | 40.2 | 7.5 | 5.3 |
| 60 | 46.5 | 43.4 | 8.2 | 6.9 |

## Conclusion

An enhanced uptake of Direct Red by cotton fibres as well as improved wet-fastness properties were observed after pre-treatment with Valine, Threonine, Proline and Histidine. This could give an effective indication towards the better use of direct dyes.

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