Dyeing of Chemically Modified Cellulose. VII. Dyeability of Cellulose Bearing Aromatic Amino, Nitro, and Acrylamidomethyl Groups

A. HEBEISH, A. WALY, A. Z. MOURSI, and F. A. ABDEL MOHDY,
National Research Centre, Textile Research Division, Dokki, Cairo, Egypt

Synopsis

The effect of introducing aromatic amino, nitro, and acrylamidomethyl groups in the cellulose molecules on the dyeing properties of two direct dyes (Chlorantine Fast Red 6BLL and Solophenyl Orange T4RL) as well as two reactive dyes, (Procion Brilliant Red M5B and Procion Brilliant Orange MG) was investigated. The extent and rate of dyeing for cellulose bearing aromatic amino groups were lower than those of nonmodified cellulose irrespective of the dye used. In addition, the extent of dyeing decreased as the amount of aromatic amino groups increased. The opposite held true for cellulose bearing acrylamidomethyl groups, particularly with direct dyes where increasing these groups caused a substantial enhancement in the dye uptake. On the other hand, subjecting cellulose to nitration reaction prior to dyeing diminished significantly its dyeability with the dyes.

INTRODUCTION

During the last few years, chemically modified celluloses have evoked considerable interest in the field of dyeing. Chemical modification of cellulose prior to dyeing changes the dyeability of cellulose, being dependent upon the type and extent of modification as well as on the nature of introduced substituent groups and/or polymer in the cellulose molecules. Previous reports[1–4] have dealt with the behavior of partially acetylated cellulose, cyanoethylated cellulose, carbamoylethylated cellulose, and partially carboxymethylated cellulose as well as cellulose grafted with polyacrylonitrile and poly(methyl methacrylate) toward dyeing with some direct and reactive dyes. Moreover, the feasibility of poly(2-methyl-5-vinyl pyridine)–cellulose graft copolymers before and after treatment with epichlorohydrin in effecting reaction of some reactive dyes with cellulose hydroxyls in absence of external alkaline catalyst has been reported.[5] Also studied was the behavior of these copolymers toward some acid and direct dyes.[5] In addition, the susceptibility of various oxidized celluloses to dyeing with some direct and reactive dyes has been examined.[6–8] In a very recent work,[9] dyeing of methylated celluose carbamate with different dyestuffs was also investigated.

In this work, the effect of changes in the chemical and physical structure of cellulose brought about by introducing aromatic amino groups, nitro groups, and acrylamidomethyl groups on the dyeability of cellulose was studied. Two direct dyes, namely, Chlorantine Fast Red 6BLL and Solophenyl Orange T4RL, as well as two reactive dyes, namely, Procion Brilliant Red M5B and Procion Brilliant Orange MG, were used.

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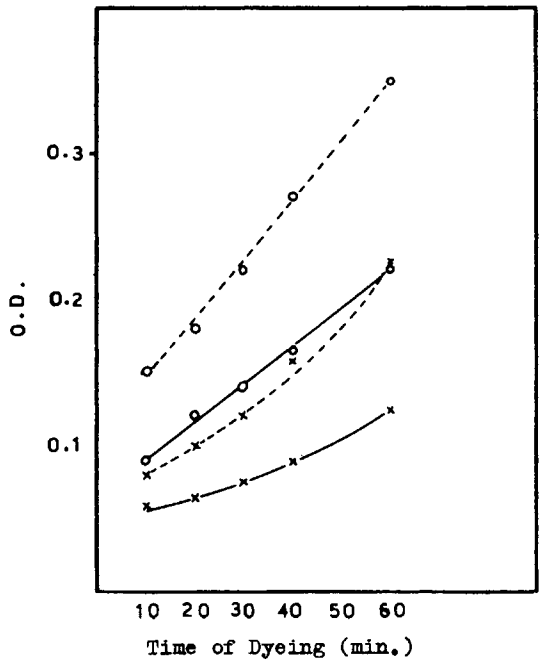

Fig. 1. Dye uptake on cellulose bearing aromatic amino groups (0.8% N) and nonmodified cellulose: (—) cellulose bearing aromatic amino groups; (- - -) nonmodified cellulose, (O) Chlorantine Fast Red 6BLL; (x) Solophenyl Orange T4RL.

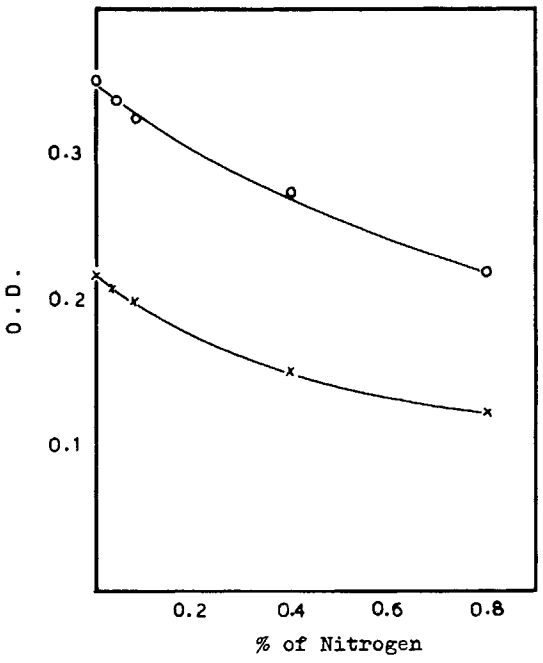

Fig. 2. Relationship between dye uptake expressed as optical density (O.D.) and the percentage of nitrogen in cellulose bearing aromatic amino groups: (O) Chlorantine Fast Red 6BLL; (x) Solophenyl Orange T4RL.

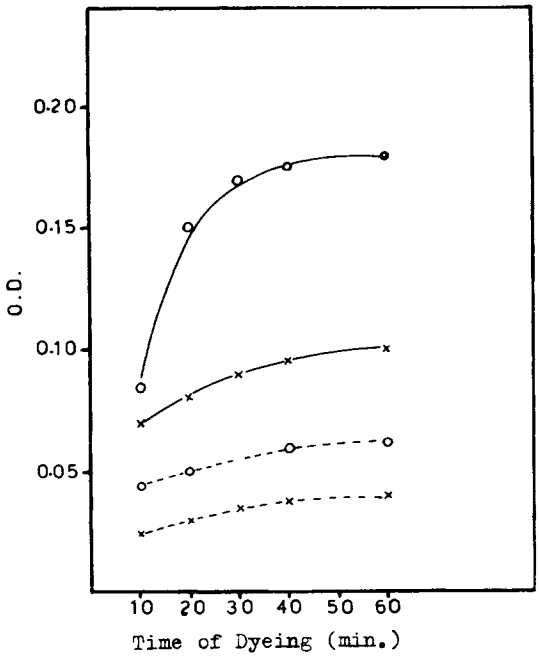

Fig. 3. Dye uptake on cellulose bearing aromatic amino groups (0.8% N) and nonmodified cellulose; (—) cellulose bearing aromatic amino groups; (- - -) nonmodified cellulose: (O) Procion Brilliant Red M5B; (x) Procion Brilliant Orange MG.

EXPERIMENTAL

Materials

Regenerated cellulose sheet (Cellophane S, Misr Rayon Co., Kafr El-Dawar, Egypt) 0.028 cm thick was used.

Modification of Cellulose

Cellulose Bearing Aromatic Amino Groups. This modified cellulose was prepared by reacting cellulose with 2,4-dichloro-6-(*p*-nitroanilino)-*s*-triazine in the presence of alkali and subsequent reduction of nitro groups to amino groups.[10] The aromatic amino groups, expressed as nitrogen, were determined by a reported method.[11]

Cellulose Bearing Nitro Groups. Preparation of cellulose bearing nitro groups was carried out by treating cellulose in a nitrating mixture consisting of nitric acid (64%), phosphoric acid (26%), and phosphorus pentoxide (10%).[12] The degree of nitration of cellulose was obtained by estimation of nitrogen content using the Kjeldahl method.

Acrylamidomethylated Cellulose. Acrylamidomethylation of cellulose was performed by reacting it with N-methylol acrylamide in the presence of NH_4Cl as catalyst.[13] The acrylamidomethyl groups, expressed as mmole double bonds/100 g cellulose, were determined according to a method described elsewhere.[14]

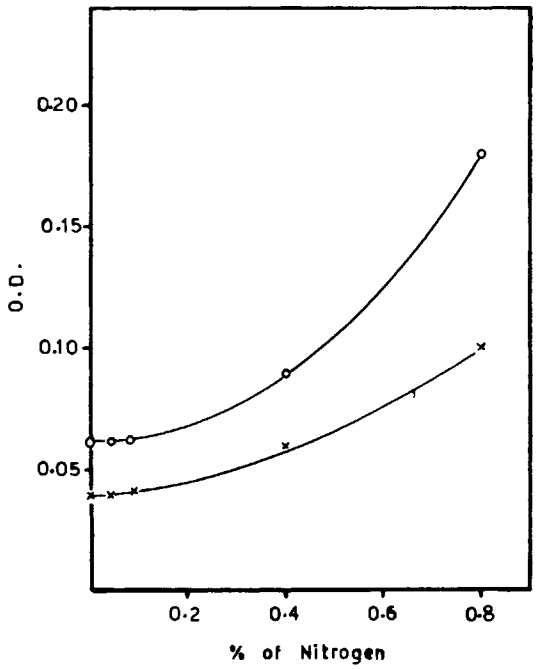

Fig. 4. Relationship between dye uptake expressed as optical density (O.D.) and the percentage of nitrogen in cellulose bearing aromatic amino groups: (○) Procion Brilliant Red M5B; (x) Procion Brilliant Orance MG.

Dyes

Commercial samples of Chlorantine Fast Red 6BLL (C.I. 29065), Solophenyl Orange T4RL (C.I. 40265), Procion Brilliant Red M5B (C.I. Reactive 2), and Procion Brilliant Orange MG (C.I. 17907) were used without further purification.

Dyeing Procedures

Dyeing with Direct Dyes. The reagents used were 1 g/l. direct dye (I) and 100 g/l. Glaubler's salt (II). The cellophane film (25 × 5 cm) was held on a stainless steel frame. The frame was then immersed in a solution containing 50 ml of solution I in 850 ml distilled water. Solution II (100 ml) was gradually added with continuous shaking. The dyeing operation was performed for different periods of time ranging from 10 to 60 min. Following the dyeing step, the sample was washed thoroughly with water, given a light soaping (1 ml/l. Nekanil LN) at the boil for 1 hr. Finally, the sample was thoroughly washed with water and air dried.

Dyeing with Reactive Dyes. The requests used were 1 g/l. reactive dye (I), 10 g/l. Glauber's salt (II), and 2.5 g/l. soda ash (III). The cellophane film (25 × 5 cm) was held on a stainless steel frame. The frame was then immersed in a solution containing 50 ml solution I in 850 ml distilled water. Solution II (100 ml) was gradually added with continuous shaking. The pH of the dyeing bath was then adjusted to pH 9.2 using solution III (25 ml). The dyeing operation

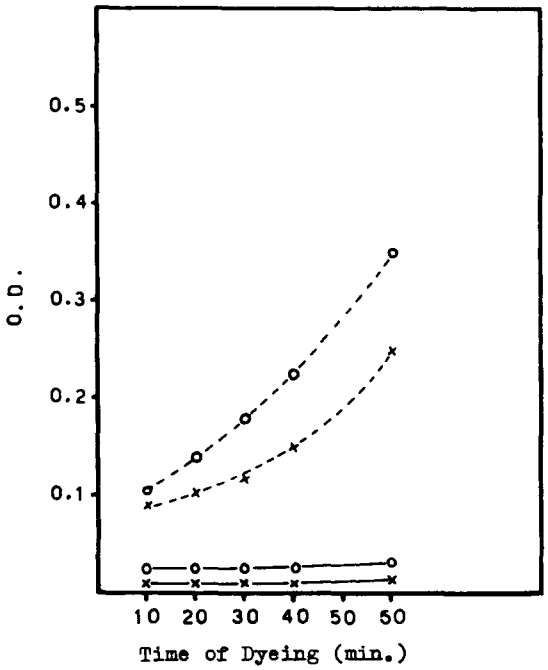

Fig. 5. Dye uptake on cellulose bearing nitro groups (1.84% N) and the nonmodified cellulose: (—) cellulose bearing nitro groups; (- - -) nonmodified cellulose; (O) Chlorantine Fast Red 6BLL; (x) Solophenyl Orange T4RL.

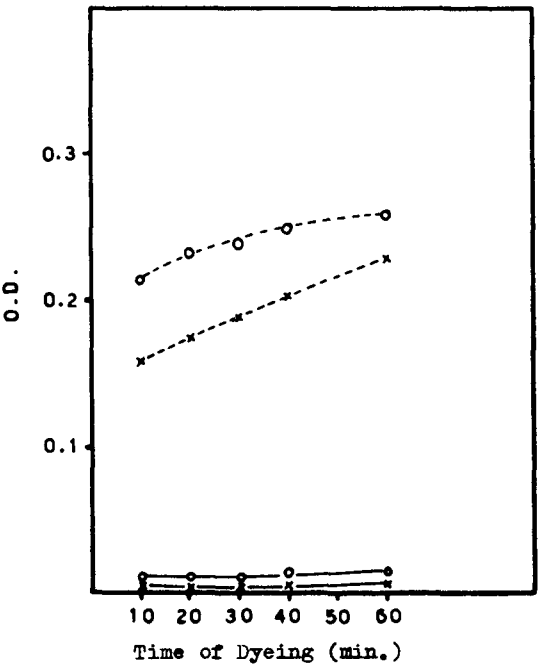

Fig. 6. Dye uptake on cellulose bearing nitro groups (1.84% N) and nonmodified cellulose: (—) cellulose bearing nitro groups; (- - -) nonmodified cellulose; (O) Procion Brilliant Red M5B; (x) Procion Brilliant Orange MG.

was performed for different periods of time ranging from 10 to 60 min. Following the dyeing step, the sample was washed thoroughly with water, given a light soaping (1 ml/l. Nekanil LN) at the boil for 1 hr, thoroughly washed with water, and finally air dried.

Measurement of Dye Uptake

The dye uptake, expressed as optical density (O.D.), was measured on a UNICAM S.P. 800 spectrophotometer at the peak of maximum absorption.

RESULTS AND DISCUSSION

Cellulose Bearing Aromatic Amino Groups

Dyeing with Direct Dyes

Cellulose bearing aromatic amino groups (0.8% N) and nonmodified cellulose were independently dyed under similar conditions with two direct dyes, namely, Chlorantine Fast Red 6BLL and Solophenyl Orange T4RL. Figure 1 depicts that with the two dyes used, cellulose bearing aromatic amino groups exhibits a lower rate of dyeing than untreated cellulose. Nevertheless, with both substrates the rate of dyeing obtained with Chlorantine Fast Red 6BLL is higher than that of Solophenyl Orange T4RL. This reflects the influence of the nature of the dye.

Introduction of aromatic amino groups in the cellulose molecule seems to perform the following functions: (a) opening up of the cellulose structure, (b) decreasing the swellability of cellulose due to their hydrophobic nature, thereby impeding diffusion of the dye, and (c) blocking some of the cellulose hydroxyls, thus decreasing its adsorptive sites. While function (a) would lead to enhancement of dyeing, functions (b) and (c) lead to a decrement of dyeing. The present data suggest that functions (b) and (c) prevail over function (a). This would account for the lower rate of dyeing observed with cellulose bearing aromatic amino groups.

Based on the foregoing it is obvious that presence of aromatic amino groups (0.8% N) in the cellulose molecule has a marked influence on its dyeing with direct dyes. It appears therefore of interest to dye cellulose bearing different amounts of aromatic amino groups with direct dyes. For this purpose, cellulose having different amounts of aromatic amino groups was dyed with the two direct dyes in question for a duration of 60 min. Results of the dye uptake are shown in Figure 2.

It is clear (Fig. 2) that increasing the amount of aromatic amino groups (expressed as % N) is accompanied by a noticeable reduction in the dye uptake, a point which substantiates and parallels the data of the dyeing rate discussed above.

Dyeing With Reactive Dyes

Figure 3 shows the change in dye uptake of two reactive dyes, namely, Procion Brilliant Red M5B and Procion Brilliant Orange MG on cellulose bearing aromatic amino groups (0.8%) as well as on nonmodified cellulose with the duration

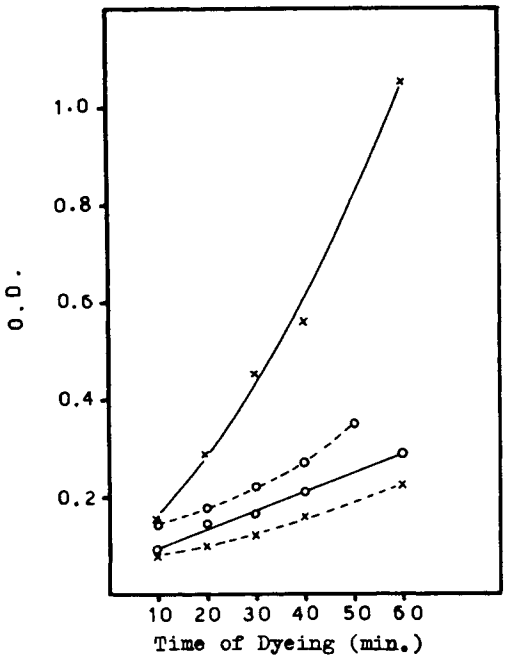

Fig. 7. Dye uptake on acrylamidomethylated cellulose (2.42 mmole double bond/1 g cellulose) and nonmodified cellulose: (—) acrylamidomethylated cellulose; (---) nonmodified cellulose; (O) Chlorantine Fast Red 6BLL; (x) Solophenyl Orange T4RL.

of dyeing. It is seen that the extent and rate of dyeing of cellulose bearing aromatic amino groups are significantly higer than those of the nonmodified cellulose. This is observed with the two reactive dyes studied, a point which is rather in full contrast with that observed with the direct dyes. However, with modified and nonmodified cellulose, Procion Brilliant Red M5B shows a much higher extent and rate of dyeing than Procion Brilliant Orange MG. This reflects the effect of the nature of the reactive dye on the extent and rate of dyeing, similar to direct dyes.

If the functions cited above for aromatic amino groups in the cellulose molecules are valid enough, the higher rate of dye uptake of reactive dyes on this modified cellulose could be interpreted in terms of opening up the cellulose structure by the presence of these groups. In addition, these groups are very likely to act as additional reactive sites for the dye. Stated in other words, the aromatic amino group facilitates reaction of the reactive dye with cellulose via (a) provision of additional active site for the dye and (b) opening up of the cellulose structure. These two functions seem to prevail over the other functions which do not favor dye uptake such as impeding diffusion and decreasing the adsorptive sites.

The data shown in Figure 4 support the fact that cellulose bearing aromatic amino groups is more amenable to reactive dyes than the nonmodified cellulose. As can be seen, the extent of dyeing increases with increasing amount of the aromatic amino groups in the cellulose molecules.

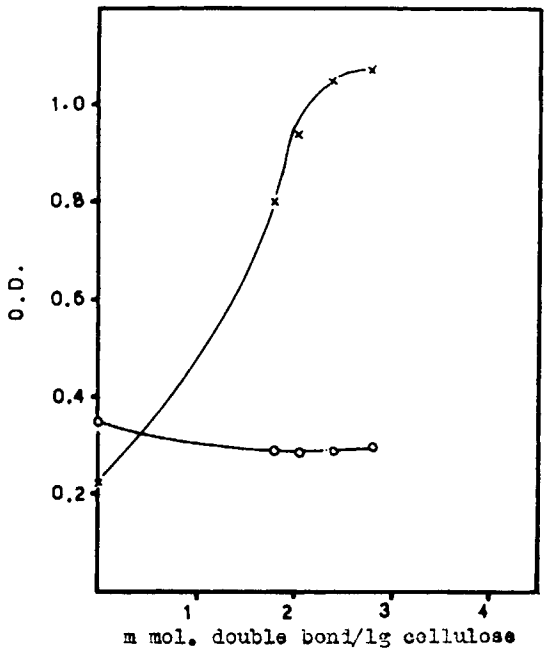

Fig. 8. Relationship between dye uptake expressed as optical density (O.D.) and amount of double bonds of acrylamidomethylated cellulose: (O) Chlorantine Fast Red 6BLL; (x) Solophenyl Orange T4RL.

Cellulose Bearing Nitro Groups

Dyeing with Direct Dyes

In Figure 5 are shown the dye uptakes obtained with partially nitrated cellulose (1.84% N) and that of the nonmodified cellulose when both substrates were independently dyed with Chlorantine Fast Red 6BLL and Solophenyl Orange T4RL. It is clear that with the two dyes the dye uptake on the nonmodified cellulose increased when the duration of dyeing was increased. A different situation is encountered with partially nitrated cellulose. With the latter, the dye uptake is much lower, as compared with the control, and does not increase as the duration of dyeing increases. This suggests that nitration causes a modification of the cellulose surface. The latter becomes impermeable. As a result diffusion of the dye into and adsorption on the cellulose matrix becomes difficult.

Dyeing with Reactive Dyes

Partially nitrated cellulose (1.84% N) was dyed under similar conditions with Procion Brilliant Red M5B and Procion Brilliant Orange MG independently. Results together with those of the nonmodified cellulose are shown in Figure 6. It is clear that the dye uptake increases with increase in the duration of dyeing in case of the nonmodified cellulose, irrespective of the dye used. The opposite holds true for the partially nitrated cellulose. With the latter, neither substantial dye uptake could be obtained nor had the duration of dyeing any significant effect, similar to direct dyes; and these effects could be explained on a similar basis.

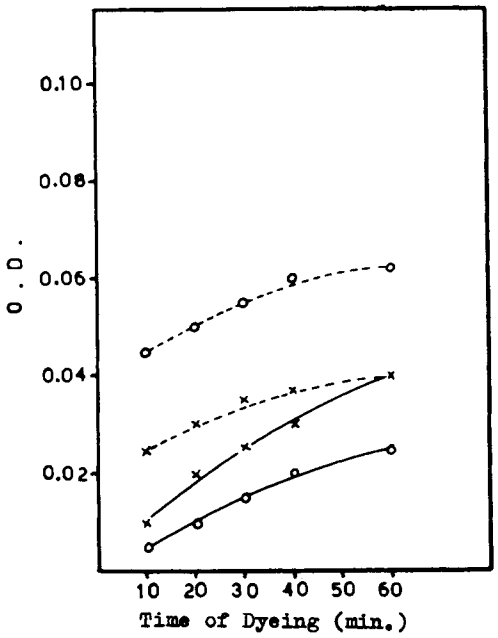

Fig. 9. Dye uptake on acrylamidomethylated cellulose (2.42 mmole double bond/1 g cellulose) and nonmodified cellulose: (—) acrylamidomethylated cellulose; (- - -) nonmodified cellulose, (O) Procion Brillant Red M5B; (x) Procion Brilliant Orange MG.

Acrylamidomethylated Cellulose

Dyeing with Direct Dyes

The dye uptakes of Chlorantine Fast Red 6BLL and that of Solophenyl Orange T4RL on acrylamidomethylated cellulose (2.42 mmole double bond/1 g cellulose) and on the nonmodified cellulose are shown in Figure 7. The extent and rate of dyeing of acrylamidomethylated cellulose are substantially higher as compared with those of the nonmodified cellulose, irrespective of the dye used. However, the dye uptake of Solophenyl Orange T4RL on acrylamidomethylated cotton is significantly greater than that of Chlorantine Fast Red 6BLL. The presence of free amino groups in the molecule of the former as well as its smaller molecular size would account for this result.

The higher extent and rate of dyeing of acrylamidomethylated cellulose, particularly when Solophenyl Orange T4RL (a dye with relatively smaller molecular size to which an amino group is attached), suggest that the acrylamidomethyl groups act as active sites for the dye. That is, addition of the labile hydrogen of the amino group of the dye to the double bond of acrylamidomethylated cellulose results in opening the double bond, with concurrent formation of a covalent bond between the dye and the modified cellulose.

Figure 8 shows the dye uptake with acrylamidomethylated celluloses having different acrylamidomethyl contents. Obviously, the dye uptake increases with increasing acrylamidomethyl groups in the modified cellulose, which substantiates the above postulation.

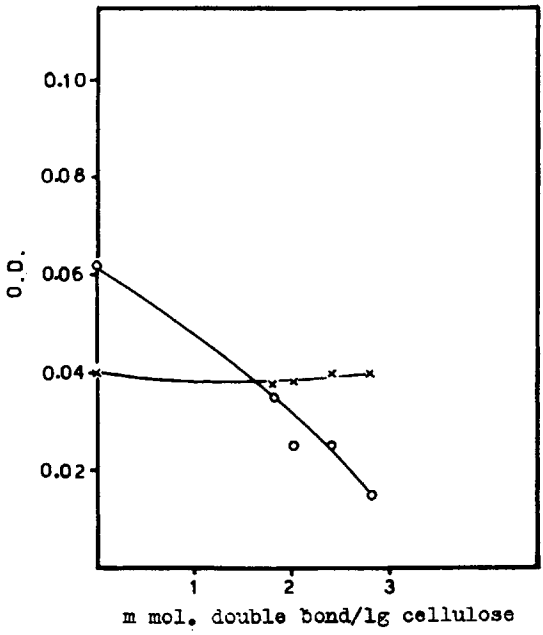

Fig. 10. Relationship between dye uptake expressed as optical density (O.D.) and amount of double bonds of acrylamidomethylated celluose: (O) Procion Brilliant Red M5B; (x) Procion Brilliant Orange MG.

Dyeing with Reactive Dyes

Figure 9 shows variation of dye uptake of Procion Brilliant Red M5B and Procion Brilliant Orange MG on acrylamidomethylated cellulose (2.42 mmole double bond/1 g cellulose) and on the nonmodified cellulose with duration of dyeing. With both dyes, the dye uptake increases with increasing duration of dyeing. This is observed regardless of the substrate used. Nevertheless, the extent and rate of dyeing obtained with acrylamidomethylated cellulose are much lower as compared to those of the nonmodified cellulose. Since dyeing with reactive dyes was carried out in alkaline medium, the lower extent and rate of dyeing could be attributed to crosslinking. Addition of cellulose hydroxyls to the double bond of the acrylamidomethyl groups results in a crosslinked cellulose with lower susceptibility to dyeing.

The effect of changing the amount of acrylamidomethyl groups in the acrylamidomethylated cellulose on the susceptibility of the latter toward dyeing is shown in Figure 10. The results of dye uptake obtained with Procion Brilliant Red M5B are in agreement with the crosslinking hypothesis, whereas those of Procion Brilliant Orange MG are not. With the latter dye, increasing the amount of acrylamidomethyl groups leaves the susceptibility of this particular dye practically intact. This contradiction is difficult to explain. However, the double functions of the acrylamidomethyl groups in crosslinking and in fixation of the hydrolyzed dye may be considered.[15] It seems that in case of Procion Brilliant Orange MG, the decrease in dye uptake brought about by crosslinking is outweighed by fixation of the hydrolyzed dye through reaction of the latter via opening the double bond of acrylamidomethyl groups.

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