Crosslinking of Cotton Cellulose in Presence of Alkyl Di-Allyl Ammonium Salts. III. Study on Pore Structure of Treated Fabrics from Dyeing Kinetics

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ABSTRACT: Two kinds of alkyl di-allyl ammonium salts (alkyl groups = methyl and propyl) as crosslinking agents are combined with dimethyloldihydroxyethyleneurea (DMDHEU) to study rate constants, structural diffusion resistance constants, and other parameters of dyeing. The dye absorptions for the various crosslinking agents are ranked DMDHEU–propyl di-allyl ammonium salt > DMDHEU–methyl di-allyl ammonium salt > DMDHEU, and the equilibrium absorption values are ranked DMDHEU–propyl di-allyl ammonium salt > DMDHEU–methyl di-allyl ammonium salt > DMDHEU. The dyeing rate constants and structural diffusion resistance constants of the finished fabrics are in the order DMDHEU–methyl di-allyl ammonium salt > DMDHEU–propyl di-allyl ammonium salt > DMDHEU; however, the activation energies are ranked inversely. The treated fabrics for DMDHEU–alkyl di-allyl ammonium salts have a larger pore structure than those for DMDHEU. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 862–866, 2005

Key words: alkyl di-allyl ammonium salt; dimethyloldihydroxyethyleneurea; rate constant; activation energies; structural diffusion resistance constant; pore structure

INTRODUCTION

Part II of this study[1] pointed that both the —OH group of the cellulose and dimethyloldihydroxyethyleneurea (DMDHEU) can be reacted with the vinyl and/or epoxy group of alkyl di-allyl ammonium salts in a pad–dry–cure process, and the physical properties and surface migration for DMDHEU–alkyl di-allyl ammonium salt treated fabrics are also changed. Many authors[2–5] mention that the pore structures of the treated fabrics are affected by varying the functional groups on the crosslinking agents.

The interest in this study is to understand the effect of the coreactants of alkyl di-allyl ammonium salts on the pore structure of the finished fabrics. The pore structure was studied by using the following diffusion equation[6,7]:

$$a = a_e[1 - \exp(-kC_0t)]^n \qquad (1)$$

$$= a_e[1 - \exp(-k't)]^n$$

where a is the absorption of the dye on the cotton in time t, a_e is the equilibrium absorption at $t \rightarrow \infty$, k is the specific rate constant, k' is the rate constant, C_0 is the concentration of cotton in a finite bath, and n is the structural diffusion resistance constant. From these values, the activation energies (ΔE^*) were also determined using the Arrhenius equation,

$$k' = \exp(-\Delta E^*/RT + e) \qquad (2)$$

where T is the absolute temperature and R is the gas constant.

The structural diffusion resistance constant and other dyeing kinetic data for the crosslinked cotton fabrics with the various DMDHEU–alkyl di-allyl ammonium salts crosslinking agent systems were determined with two direct dyes. These were used to study the pore properties of those treated fabrics.

EXPERIMENTAL

Desized, scoured, and bleached cotton fabric in 20s × 20s ends (60) and picks (60) were used in this study.

The crosslinking agents were DMDHEU and alkyl di-allyl ammonium salts, which were synthesized with the method described by Töpfl.[8] The alkyl groups were —CH_3 and —C_3H_7, respectively.

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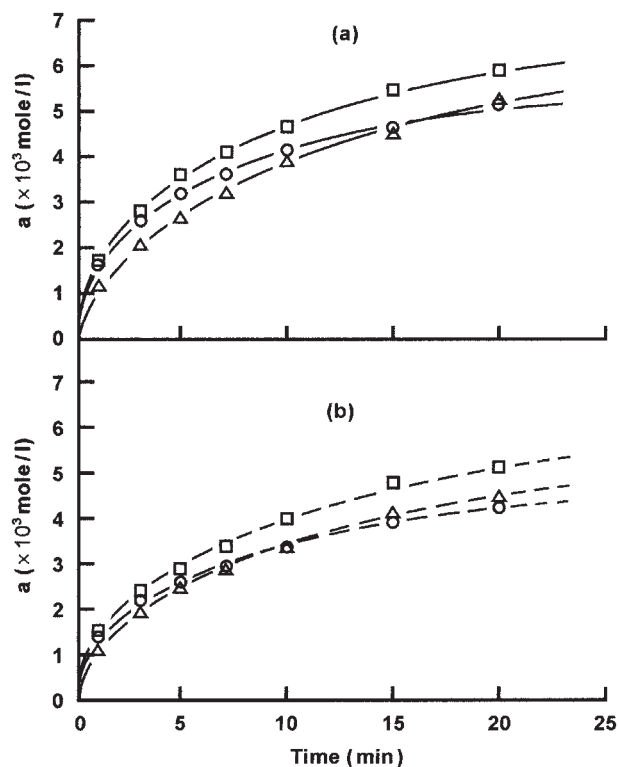
Figure 1 The rates of dye (CI Direct Red 81) adsorption for fabrics treated with DMDHEU at (–○–) 70°C and (···○···) 50°C/DMDHEU-methyl di-allyl ammonium salt at (–△–) 70°C and (···△···) 50°C, and DMDHEU-propyl di-allyl ammonium salt at (–□–) 70°C and (···□···) 50°C.

DMDHEU

Alkyl di-allyl ammonium salts
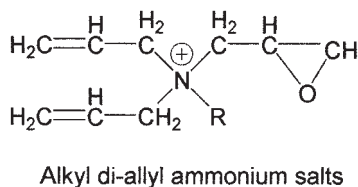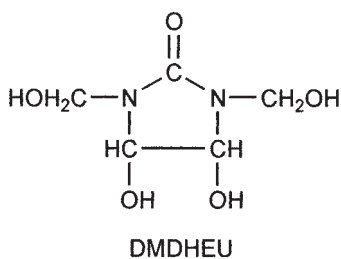
Ammonium sulfate was reagent grade, as were the other chemicals.

The cotton fabric samples were padded twice to about 90% wet pickup with a freshly prepared (4%, w/w) aqueous solution of DMDHEU in the presence of alkyl di-allyl ammonium salts and the ammonium sulfate catalyst. The alkyl di-allyl ammonium salts and the catalyst concentrations were 0.50 and 0.10 times the crosslinking agent solid concentration, respec-

tively. Padded fabrics were dried at 80°C for 5 min, cured at 160°C for 3 min, soaped, washed, and dried.

The crosslinked cotton fabrics were cut into approximate 0.5-cm^2 pieces and dyed with CI Direct Red 111 and CI Direct Red 81 (0.05 g/L dye, 10 g/L NaCl) at a 60:1 liquor ratio. The dyeing temperatures were 50, 60, and 70°C, which were kept constant in a water bath. The dye solution and cotton fabric were stirred slowly using a magnetic stirrer. After selected time intervals, the dye concentration in the dye solution was measured directly on a Hitachi U-3010 spectrophotometer.

Treated fibers were brought to a boil for 1 h in a 50 vol % aqueous solution of methanol containing 0.5% wetting agent (Triton X-100) and allowed to cool and soak overnight in this wetting solution. Then, the wet fibers were laid on a glass slide and covered immediately with nitrocellulose, which had been dissolved in acetone. The cross sections of the treated fibers were observed with a scanning electron micrograph.

RESULTS AND DISCUSSION

Figure 1(a) shows the rates of dye absorption at 70°C (Direct Red 81) of the cotton crosslinked with DMDHEU, DMDHEU–methyl di-allyl ammonium salt, and DMDHEU–propyl di-allyl ammonium salt. From this
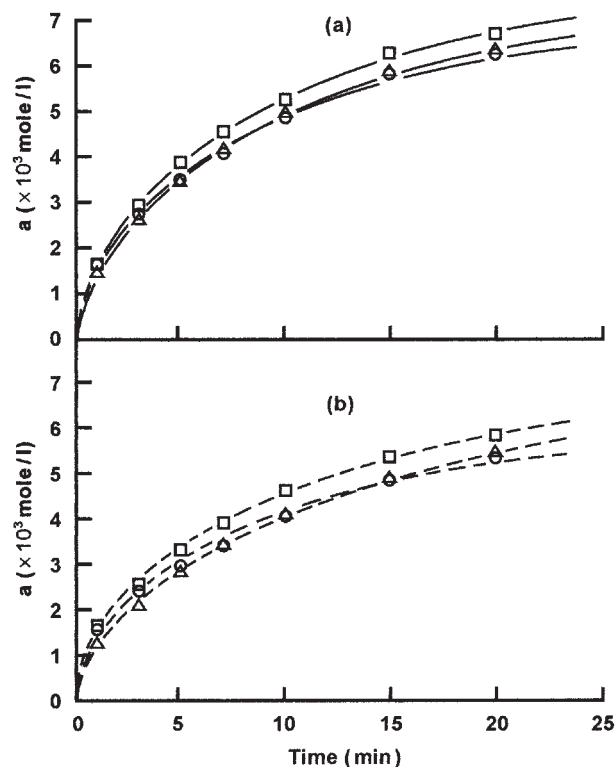
Figure 2 The rates of dye (CI Direct Red 111) adsorption for fabrics treated with DMDHEU at (–○–) 70°C and (···○···) 50°C/DMDHEU-methyl di-allyl ammonium salt at (–△–) 70°C and (···△···) 50°C, and DMDHEU- propyl di-allyl ammonium salt at (–□–) 70°C and (···□···) 50°C.
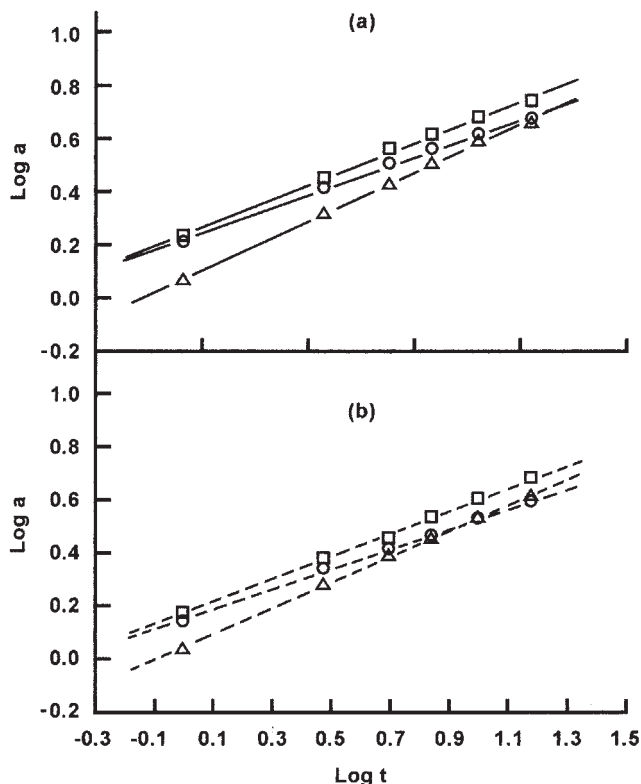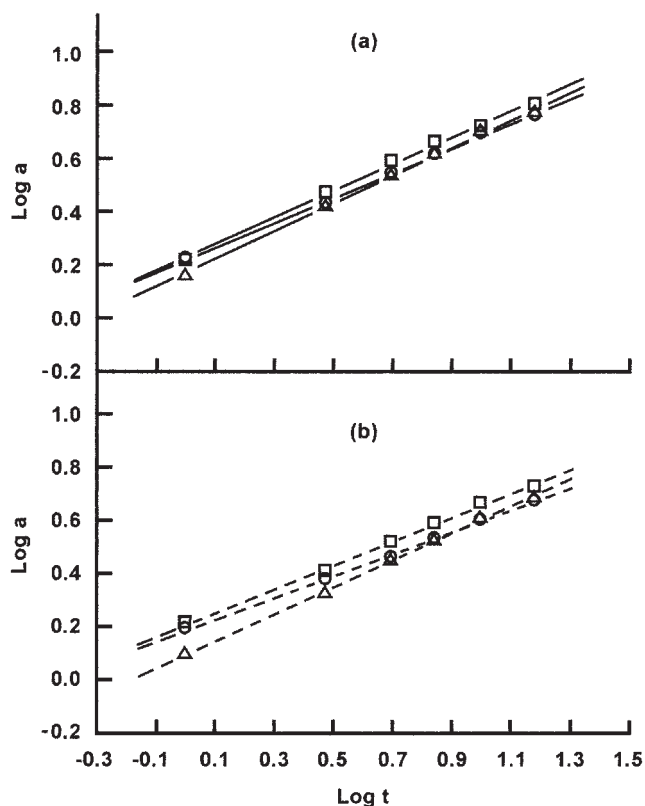
Figure 3 Plots of log *a* versus log *t* for fabrics treated with DMDHEU at (–○–) 70°C and (· · ·○· · ·) 50°C DMDHEU-methyl di-allyl ammonium salt at (–△–) 70°C and (· · ·△· · ·) 50°C, and DMDHEU-propyl di-allyl ammonium salt at (–□–) 70°C and (· · ·□· · ·) 50°C and dyed with CI Direct Red 81.

figure, we can find that the type of the dye absorptions for DMDHEU–alkyl di-allyl ammonium salts are different from that for DMDHEU. At the initial dyeing time duration, the dye absorptions for the various crosslinking agents are ranked DMDHEU–propyl di-allyl ammonium salt > DMDHEU > DMDHEU–methyl di-allyl ammonium salt. Figure 1(b) shows that the rates of dye absorption at 50°C for the three treated fabrics have a similar tendency. The higher dye absorption values for DMDHEU–propyl di-allyl ammonium salts may be caused by the reaction between the anionic ion of the direct dye and the cationic ion of the propyl di-allyl ammonium salts or the hydrophobic bonding between the hydrophobic groups (aryl group, etc.) of the direct dye and the longer propyl group of the propyl di-allyl ammonium salt. A previous study[9] showed that the higher hydrophobic bonding between the dye and fiber increases the dye absorption values.

The rates of Direct Red 111 dye absorption of the cotton crosslinked with three crosslinking agent systems at 70 and 50°C in Figure 2(a,b) show similar tendencies compared with those shown in Figure 1(a,b).

Figure 3(a) shows the linear relationships between the logarithmic values of dye (CI Direct Red 81) absorption (log *a*) at 70°C and the logarithmic values of the time intervals of dyeing (log *t*) over the duration of the initial dyeing time, and Figure 3(b) shows similar relationships at 50°C. From these results, we believe that the use of the diffusion kinetic equation reported by Chrastil et al.[6,7] to study the a_e, k', and n (the index of the pore structure) of the various treated cotton fabrics is suitable. Figure 4(a,b) shows similar relationships for CI Direct Red 111. These data are listed in Table I.

Table I shows that the equilibrium absorption values of the three finished fabrics for the various agent systems are in the order DMDHEU–propyl di-allyl ammonium salt > DMDHEU–methyl di-allyl ammonium salt > DMDHEU. The differences in the values of a_e among the DMDHEU–propyl di-allyl ammonium salt, DMDHEU–methyl di-allyl ammonium salt, and DMDHEU crosslinked fabrics are not significant for the two dyes that were used. However, the differences in the values of a_e between Direct Red 81 and Direct Red 111 for the same crosslinked fabric and dyeing temperature are significant. Under the same dyeing

Figure 4 Plots of log *a* versus log *t* for fabrics treated with DMDHEU at (–○–) 70°C and (· · ·○· · ·) 50°C/DMDHEU-methyl di-allyl ammonium salt at (–△–) 70°C and (· · ·△· · ·) 50°C, and DMDHEU-propyl di-allyl ammonium salt at (–□–) 70°C and (· · ·□· · ·) 50°C and dyed with CI Direct Red 111.

TABLE I
Values of Equilibrium Adsorption, Rate Constant, Structural Diffusion Resistance Constant, and Activation Energy of Treaded Fabrics with DMDHEU-Alkyl Di-allyl Ammonium Salts Systems

Direct dye CI no.	Molecular weight (g/mol)	Dyeing temp. (°C)	DMDHEU				DMDHEU-methyl di-allyl ammonium salt				DMDHEU-propyl di-allyl ammonium salt			
			$a_e \times 10^{-3}$ M	$k' \times 10^{-3}$ (min^{-1})	n	ΔE^* (kcal/mol)	$a_e \times 10^{-3}$ M	$k' \times 10^{-3}$ (min^{-1})	n	ΔE^* (kcal/mol)	$a_e \times 10^{-3}$ M	$k' \times 10^{-3}$ (min^{-1})	n	ΔE^* (kcal/mol)
81	676	50	12.077	3.557	0.379	8.536	12.296	7.178	0.486	4.930	12.706	6.707	0.423	5.388
		60	11.695	5.503	0.387		12.132	9.968	0.490		12.542	8.971	0.429	
		70	11.367	7.721	0.392		12.023	11.213	0.504		12.405	10.935	0.433	
111	349	50	14.789	4.352	0.412	9.427	15.013	8.039	0.509	5.660	15.349	6.911	0.445	6.908
		60	14.565	6.521	0.429		14.789	10.802	0.515		15.125	9.153	0.458	
		70	14.397	10.258	0.467		14.565	13.436	0.521		14.957	12.958	0.496	

The data for the rate constant were obtained from a dyeing time interval of 10 min.
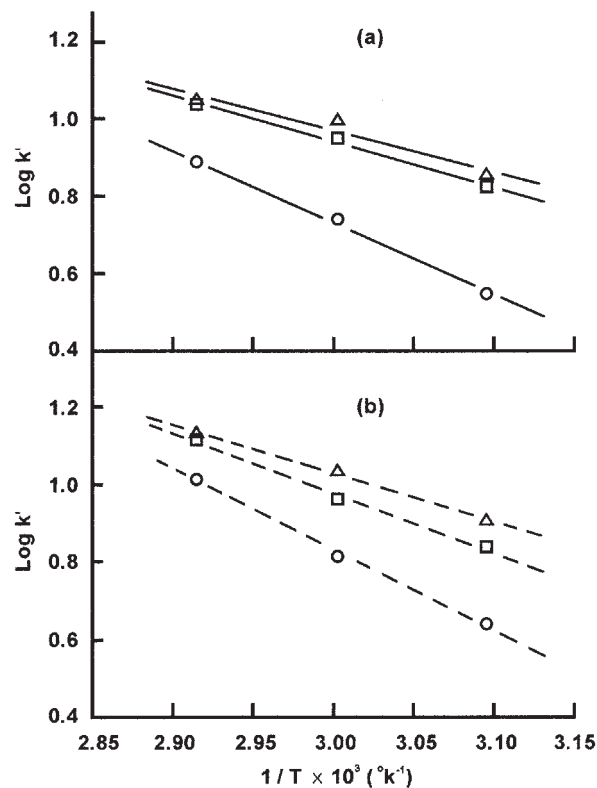

Figure 5 Arrhenius plots of the (○) DMDHEU, (□) DMDHEU-methyl di-allyl ammonium salt, and (△) DMDHEU-propyl di-allyl ammonium salt treated fabrics dyed with (a) CI Direct Red 81 and (b) CI Direct Red 111.

temperature, the a_e values of Direct Red 111 are higher than those of Direct Red 81, which are inversely related to the molecular weight of the dyes. We believe that the significant differences of the a_e values between the two dyes are caused by the higher diffusion mobility of the lower molecular weight of the dye. These results are the same as a previous study.[10]

For all cases, the rate constants are increased with the rise of the dyeing temperature. Rate constants for the three finished fabrics (for a same direct dye and a same dyeing temperature) were DMDHEU–methyl di-allyl ammonium salt > DMDHEU–propyl di-allyl ammonium salt > DMDHEU. These results may be caused by the pore structure of crosslinked fabrics,[9] and the dependence of the absorption on the higher molecular weight of the dye.

The structural diffusion resistance constants are only slightly increased with increasing dyeing temperature (Table I). Table I shows that for all cases (two direct dyes and three dyeing temperatures) the structural diffusion resistance constants for the three finished fabrics were in the order DMDHEU–methyl di-allyl ammonium salt > DMDHEU–propyl di-allyl ammonium salt > DMDHEU. Two reports[11,12] revealed that the crosslinks decrease the structural diffusion resistance constant. In addition, the structural diffusion resistance constant values
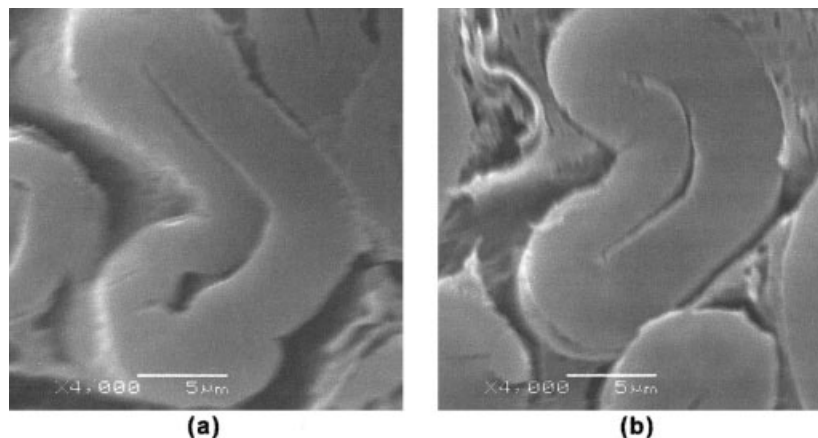
Figure 6 The expansion patterns (SEM) of cross sections of the (a) 5% DMDHEU treated and (b) 5% DMDHEU-propyl di-allyl ammonium salt treated fiber.

are increased with the decrease of the molecular weight of the dye for all cases. Those results agree with the results of another report,[9] and they indicates that the pore structure of the crosslinked cotton is changed with the addition of alkyl di-allyl ammonium salts and the length of the alkyl group of the alkyl di-allyl ammonium salts of the DMDHEU–alkyl di-allyl ammonium salts crosslinking agent systems.

Arrhenius plots (three treated fabrics and two dyes) are shown in Figure 5(a,b). The activation energies from Figure 5 are also listed in Table I. The activation energies for the three finished fabrics (dyed with a same direct dye) are DMDHEU > DMDHEU–propyl di-allyl ammonium salt > DMDHEU–methyl di-allyl ammonium salt. This ranking also reflects the pore structure of the finished fabrics. Moreover, the activation energies for the two direct dyes (the same finished fabric) are ranked Direct Red 111 > Direct Red 81, reflecting the molecular weight of the dyes (and the pore structure of the finished fabrics).

The SEM expansion patterns of cross section of the 5% DMDHEU treated and 5% DMDHEU–propyl di-allyl ammonium salt treated fibers are shown in Figure 6(a,b). The figure shows that the degree of expansion of the DMDHEU treated fiber is lower than that of the DMDHEU–propyl di-allyl ammonium salt treated fiber. These results agree with the data for the structural diffusion resistance constants and the rate constants of dyeing listed in Table I.

CONCLUSIONS

In this study, DMDHEU and DMDHEU–alkyl di-allyl ammonium salts were used to treat cotton fabrics for the examination of rate constants, structural diffusion resistance constants, and other parameters of dyeing. The results show that the dye absorptions of the treated fabrics for the various crosslinking agents are ranked

DMDHEU–propyl di-allyl ammonium salt > DMDHEU > DMDHEU–methyl di-allyl ammonium salt, and the equilibrium absorption values are ranked DMDHEU–propyl di-allyl ammonium salt > DMDHEU–methyl di-allyl ammonium salt > DMDHEU under the same dyeing temperature. Both the dye absorption and equilibrium absorption values for the two direct dyes are in the order Direct Red 111 > Direct Red 81. The dyeing rate constants and structural diffusion resistance constants of the three finished fabrics (for the same direct dye and the same dyeing temperature) show the rank of DMDHEU–methyl di-allyl ammonium salt > DMDHEU–propyl di-allyl ammonium salt > DMDHEU; however, the activation energies (dyed with the same direct dye) are ranked inversely. In contrast, the dyeing rate constants, structural diffusion resistance constants, and activation energies for Direct Red 111 are higher than those for Direct Red 81. The swelling property of the DMDHEU treated fiber is *lower* than that of DMDHEU–propyl di-allyl ammonium salt.

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