

# Crosslinking of Cotton Cellulose in the Presence of Serine and Glycine. II. Pore Structures and Agent Distribution

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**ABSTRACT:** Serine and glycine are selected as coreactants to combine with dimethylol-dihydroxyethyleneurea (DMDHEU). We found that the pore structures of DMDHEU-crosslinked cottons are changed. DMDHEU alone has lower values of equilibrium absorption, structural diffusion resistance constant, and rate constant, but higher value of activation energy than do DMDHEU-serine and DMDHEU-glycine. On the other hand, DMDHEU-serine has higher values of structural diffusion resistance constant and lower values of equilibrium absorption and rate constant than does DMDHEU-glycine; however, the hydroxyl group contained in serine has the higher affinity toward direct dye resulting

in the decrease in the value of activation energy. The expansion patterns of cross section show that the degree of the expansion of the DMDHEU-crosslinked fiber is lower than that of the DMDHEU-serine- and DMDHEU-glycine-crosslinked fibers. The distribution of crosslinking agents on the crosslinked fabrics reveals the slightly higher surface distribution of DMDHEU-serine and DMDHEU-glycine.

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**Key words:** activation energy; adsorption; crosslinking; kinetics; fibers

## INTRODUCTION

From the absorbing bands of methylol group ( $-\text{CH}_2\text{OH}$ ) for dimethylol-dihydroxyethyleneurea (DMDHEU) and primary amino and carboxyl acid groups for aspartic acid or serine and those absorbing bands changed for cured DMDHEU-aspartic acid or DMDHEU-serine of the infrared spectra showed on our previous study,<sup>1,2</sup> it was found that the  $-\text{OH}$  group of DMDHEU could react with the functional groups of aspartic acid and serine. One of those results<sup>2</sup> alluded that the higher WCRA of the DMDHEU-serine-treated fabric was caused by the higher condensation reaction between the *N*-methylol group of DMDHEU and the reactive functional groups of the serine, especially hydroxyl group. Additionally, our previous study<sup>2</sup> also showed that the specific reaction rate constant for DMDHEU-serine was lower than that for DMDHEU alone, which was attributed to the lower crosslinking reaction ability of serine and the buffering effect caused from the complex formation between  $\alpha$ -amino acid molecule and aluminum ion catalyst. Some studies<sup>3,4</sup> revealed that the crosslinking activity between amino and carbonyl acid groups of  $\alpha$ -amino acid and the hydroxyl group of cellulose is

significantly lower than that between *N*-methylol group of crosslinking agent and the hydroxyl group of cellulose, however the crosslinking activity between amino group of amino acid and *N*-methylol group of crosslinking agent is significantly higher than that between *N*-methylol group and *N*-methylol group of crosslinking agent. Those phenomena strongly suggested that the pore structure caused by the crosslinking of DMDHEU- $\alpha$ -amino acid might be different from that for DMDHEU alone. Many other authors<sup>5–8</sup> mentioned that the pore structures of the treated fabrics are affected by varying the functional groups of crosslinking agents. We are interested in the effect of the coreactants of the  $\alpha$ -amino acids having one carboxylic acid group and one amine group on the pore structure of the treated fabrics, which has never been reported. Meanwhile, the effect of the hydroxyl group of  $\alpha$ -amino acid on the pore structure of the treated fabrics will also be investigated in this study. To achieve this goal, serine and glycine were selected to combine with DMDHEU as crosslinking agents, which probably have different degrees of condensation reaction to create different pore structures and other properties in the treated fabrics. Additionally, detailed information about the agent distribution on the DMDHEU-serine-treated and DMDHEU-glycine-treated fabric is lacking.

Here, the direct dye, C. I. Direct red 81 having molecular weight of 676 g/mol, will be used to study

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the pore structure of the DMDHEU-serine- and DMDHEU-glycine-treated fabrics. We studied the pore structure by using the following diffusion equation:<sup>9-12</sup>

$$a = a_e[1 - \exp(-kC_0t)]^n = a_e[1 - \exp(-k't)]^n, \quad (1)$$

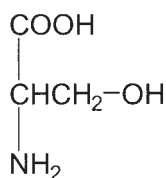
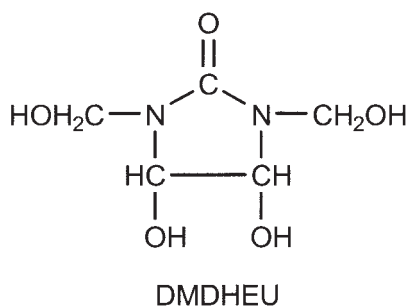
where  $a$  is the absorption of the dye on cotton in time  $t$ ,  $a_e$  is the equilibrium absorption at  $t \rightarrow \infty$ ,  $k$  is the specific rate constant,  $k'$  is the rate constant,  $C_0$  is the concentration of cotton in a finite bath, and  $n$  is the structural diffusion resistance constant. The higher value of  $n$  represents the larger pore size of the treated fabric. The SEM pictures will also be used to confirm the state of the pore structures of DMDHEU and DMDHEU- $\alpha$ -amino acids-treated fibers. On the other hand, a negative staining method described by Rowland et al.<sup>8,13,14</sup> will be used to determine the distribution of agents on the treated fabrics.

## EXPERIMENTAL

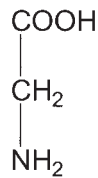
### Materials

In this study, we used desized, scoured, and bleached cotton fabric with 60 ends and 60 picks. The count of fiber yarn was 32.

The crosslinking agents used were DMDHEU (dimethylol-dihydroxyethyleneurea, supplied by Cyanamid, Taipei, Taiwan) and  $\alpha$ -amino acids used were glycine (supplied by Sigma-Aldrich Laborchemikalien, Wunstorf, Germany) and serine (supplied by Sigma, St. Louis, MO), respectively.



Serine



Glycine

Aluminum sulfate was reagent grade, as were the other chemicals.

### Examination of dyeing kinetics

The cotton fabric samples were padded twice to about 90% wet pickup with freshly prepared (3% w/w) aqueous solution of DMDHEU in the presence of  $\alpha$ -amino acids (the mole ratio of DMDHEU to  $\alpha$ -amino acids was 3 to 1) and the ammonium sulfate catalyst. To avoid the blocking effect of direct dye during pore structure determination, the relative lower concentration (3 wt %) of DMDHEU was selected. The concentration of coreactants was used according to our previous study<sup>2</sup> to have the coherence of the research of series. The catalyst concentration was 0.10 times the crosslinking agent solid concentration. Padded fabrics were dried at 80°C for 5 min, cured at 160°C for 3 min, soaped, washed, and dried.

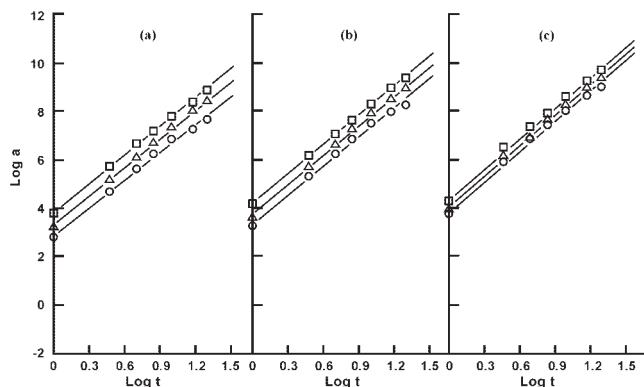
The crosslinked cotton fabrics (about 2.0 g) were cut into pieces of approximately 0.5 cm<sup>2</sup> and dyed with C. I. Direct Red 81 (dye: 0.12 g/L, NaCl: 10 g/L) at a 60:1 liquor ratio. Dyeing temperatures were 50, 60, and 70°C and were kept constant in a water bath. The dye solution and cotton fabric 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 (Hitachi, Tokyo, Japan).

### Examination of agent distribution

For the investigation of agent distribution on the treated fabrics, the 2, 4, 6, and 8% (w/w) DMDHEU and the mixture of DMDHEU/ $\alpha$ -amino acids (the mole ratio of DMDHEU to  $\alpha$ -amino acids was 3 to 1)-treated fabric samples were dyed with C. I. Direct Red 81 (0.5 g/L, 10 g/L NaCl) under a liquor ratio of 60:1 at 90°C for 40 min. The  $K/S$  values (depth of color of the various treated fabrics) were measured at a color intensity instrument of SF-600 (Datacolor, Lawrenceville, NJ), and the  $[D]_f$  values (g dye/kg cotton) were determined spectrophotometrically with U-3010 spectrophotometer (Hitachi) after extraction the dyed fabrics with pyridine/water (1/3) at 60°C.  $K$  is the coefficient of absorption,  $S$  is the coefficient of scattering,  $K/S$  is color intensity calculated from the equation  $K/S = (K/S)_{\text{dye}} - (K/S)_{\text{whiter}}$ , and  $[D]_f$  (g dye/kg cotton) is the dye content of the finished fabric, determined spectrophotometrically after extraction with pyridine/water (1/3) at 60°C.

### Observation of scanning electron micrograph

Treated fibers were boiled in a 50% (by volume) aqueous solution of methanol containing 0.5% wetting agent (Triton X-100) for 1 h 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



**Figure 1** The relationships between the logarithmic values of the dye (direct red 81) absorption ( $\log a$ ) and the logarithmic values of the time intervals of dyeing ( $\log t$ ) of the DMDHEU-, DMDHEU-serine-, and DMDHEU-glycine-crosslinked fabrics dyed under (a) 50°C, (b) 60°C, and (c) 70°C, separately.  $\circ$  = DMDHEU,  $\triangle$  = DMDHEU-serine,  $\square$  = DMDHEU-glycine.

acetone. The cross sections of the treated fibers were observed by a scanning electron micrograph (SEM, JSM-6335F JEOL, Tachigawa, Japan).

## RESULTS AND DISCUSSION

### Dyeing kinetics and pore structure

Figure 1(a–c) show the rates of dye absorption of the crosslinked cotton with DMDHEU alone, DMDHEU-serine, and DMDHEU-glycine. They show the linear relationships between the logarithmic values of the dye (direct red 81) absorption ( $\log a$ ) under different temperatures and the logarithmic values of the time intervals of dyeing ( $\log t$ ) over the initial dyeing time duration. From those results of linear relationships, we believe that the use of the diffusion kinetic equation reported earlier<sup>9–12</sup> to study the equilibrium absorption ( $a_e$ ), rate constant ( $k'$ ), and structural diffusion resistance constant ( $n$ , the index of the pore structure) of the various treated cotton fabrics is suitable.

Several data obtained from the dyeing kinetics of eq. (1) are all listed in Table I.

Table I shows that the equilibrium absorption values of the direct red dye for the DMDHEU-serine and DMDHEU-glycine crosslinked fabrics are higher than that for DMDHEU-treated fabric at a given temperature. This result may be caused by the degrees of condensation reaction between DMDHEU and the two amino acids being higher than that between DMDHEU and DMDHEU to form a loose crosslink. In addition, it can also be found that the equilibrium absorption value for the DMDHEU-glycine-crosslinked fabric is higher than that for DMDHEU-serine-treated fabric at a given temperature. This may be caused by the different degrees of condensation reaction between DMDHEU-serine and DMDHEU-glycine. Serine has a methylol functional group except one amino group and one carboxylic acid functional group, but glycine has only one amino group and one carboxylic acid group. It is well known that the methylol group is an active functional group for reacting with *N*-methylol group of DMDHEU, and so the condensation between DMDHEU/serine and DMDHEU/glycine and the pore structure are surely different from each other.

For all cases, the equilibrium absorption values are decreased and the rate constants are increased with the raising of dyeing temperature. The sizes of the pores of the dyed materials are well-known to increase with the increasing of dyeing temperature. This phenomenon will increase the migration of dye molecule in the matrix of dyed materials to decrease the values of equilibrium absorption.<sup>15</sup> Meanwhile, the higher migration of dye molecule in the dyed matrix will increase the values of rate constant. Additionally, rate constants for the three crosslinked fabrics that were dyed at a same dyeing temperature show the rank of DMDHEU-glycine > DMDHEU-serine > DMDHEU. Those results may be caused by the difference of pore structure of the various crosslinked cotton fabrics and

**TABLE I**  
The Values of Equilibrium Adsorption, Rate Constant, Structural Diffusion Resistance Constant, and Activation Energy of the Various Fabrics Separately Treated with DMDHEU, DMDHEU-Serine, and DMDHEU-Glycine

Crosslinking agents	Dyeing temp. (°C)	$a_e \times 10^{-3}$ (M)	$N$	$K'$ ( $\times 10^{-3} \text{ min}^{-1}$ )	$\Delta E^*$ (Kcal/mol)
DMDHEU	50	8.87	0.38	20.00	13.06
	60	8.78	0.39	35.15	
	70	8.72	0.40	65.56	
DMDHEU-serine	50	9.28	0.40	33.50	10.16
	60	9.21	0.41	53.29	
	70	9.16	0.42	84.38	
DMDHEU-glycine	50	9.63	0.39	35.85	11.28
	60	9.42	0.40	66.63	
	70	9.31	0.41	99.70	

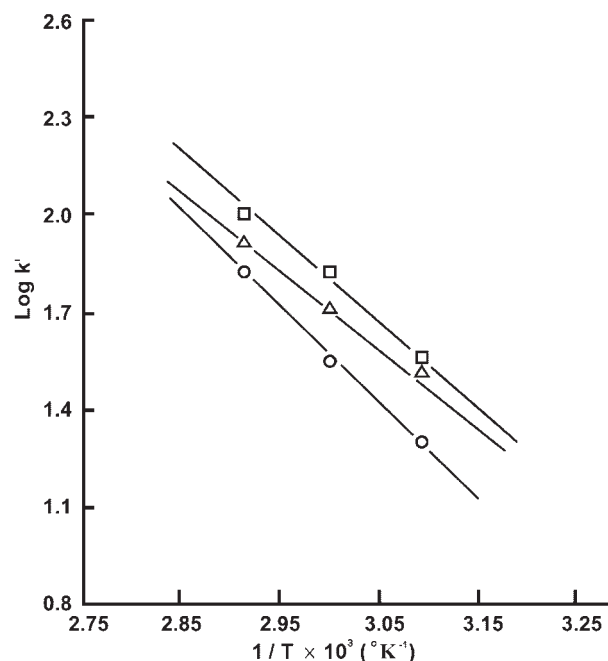
the bonding dependence during the dye absorption.<sup>15,16</sup>

Structural diffusion resistance constants are only slightly changed with the increasing of dyeing temperature (Table I). Table I also shows that for all cases (three dyeing temperatures), structural diffusion resistance constants for the three crosslinked fabrics follow the following order of DMDHEU-serine > DMDHEU-glycine > DMDHEU. Several reports<sup>9,13</sup> revealed that the crosslinks would decrease the structural diffusion resistance constant. Those results agree with the results of another report<sup>15</sup> and indicate that the pore structure of the crosslinked cotton fabrics is changed with the addition of amino acids to combine with DMDHEU as crosslinking agent. It is suggested that the coreactant amino acids will react with crosslinking agent (DMDHEU) to create a loose crosslink, i.e., a larger pore structure. The slightly higher values of the structural diffusion resistance constant for the DMDHEU-serine-crosslinked cotton as compared with those for DMDHEU-glycine may be caused by the higher degree of condensation between DMDHEU and serine due to the presence of hydroxyl group in serine, which is not present in glycine.

From the data of structural diffusion resistance constants and the equilibrium absorption under specific dyeing time duration, we can obtain the value of rate constant at the dyeing time interval, which were listed in Table I. In this study, this value of time interval was set as 15 min. From those data, it was found that the value of rate constant for DMDHEU-crosslinked cotton is lower than that for DMDHEU-serine and DMDHEU-glycine, however the data for DMDHEU-serine is lower than that for DMDHEU-glycine at a given dyeing temperature. This result may be due to the difference of pores formed from the different degrees of condensation of crosslinking agents discussed on the earlier section. Additionally, the affinity between the dyed materials and dye molecules will also change the rate constant of dyeing.<sup>15</sup>

Arrhenius plots (three crosslinked cotton fabrics) for the direct red 81 are shown in Figure 2. The activation energies ( $\Delta E^*$ ) from the figures are also listed in Table I. The activation energies for the three crosslinked fabrics are ranked as follows: DMDHEU > DMDHEU-glycine > DMDHEU-serine. This ranking also agrees with the pore structure of the crosslinked fabrics that is the structural diffusion resistance constant. The larger the pore (loose crosslinks) the lower is the value of activation energy.

Broadly, the outline of the difference of pore structures between serine- and glycine-combined crosslinking agents and DMDHEU can be described as following. DMDHEU alone has higher crosslinking reaction with cellulose molecules, therefore has

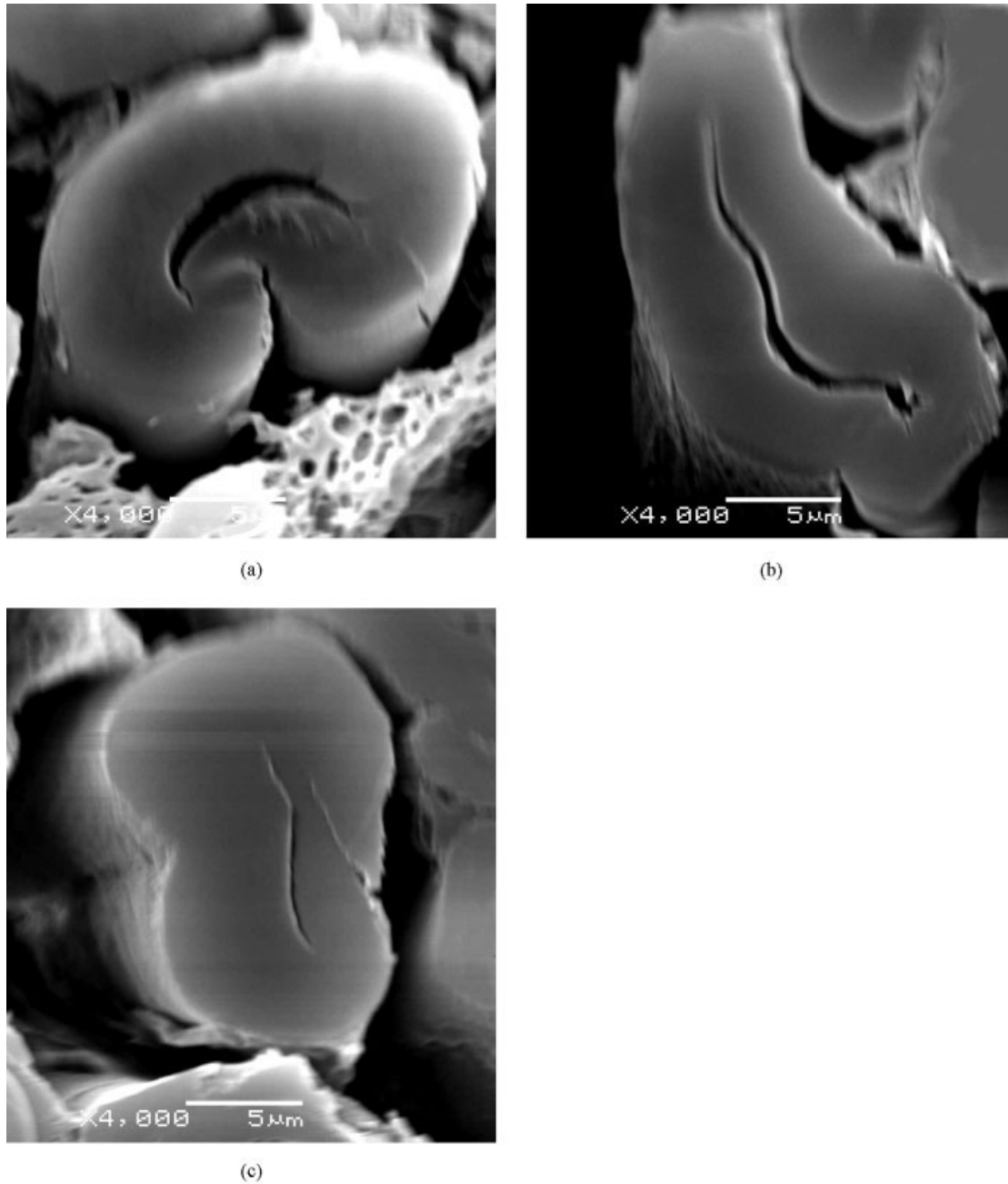


**Figure 2** Arrhenius plots of the  $\circ$ :DMDHEU-,  $\Delta$ :DMDHEU-serine-, and  $\square$ : DMDHEU-glycine-crosslinked fabrics dyed with direct red 81.

tighter crosslinks to decrease the value of equilibrium absorption, structural diffusion resistance constant, and rate constant, but increase the value of activation energy. At the same time, those data of equilibrium absorption, structural diffusion resistance constant, and rate constant for DMDHEU alone are lower than those for DMDHEU-amino acids (serine and glycine) for the looser crosslinks of DMDHEU-amino acids crosslinked fabrics, which are caused by the higher condensation reaction for DMDHEU-amino acids crosslinking agents. On the other hand, the higher degree of condensation of DMDHEU-serine than that of DMDHEU-glycine makes the looser crosslinks to have higher values of structural diffusion resistance constant and lower values of equilibrium absorption for migration effect. However, the hydroxyl group in serine should have the higher affinity with direct dye (hydrophilic bonding) to block the penetration of direct dye molecules in the dyed matrix therefore having the lower values of rate constant. The higher affinity between direct dye molecules and DMDHEU-serine-crosslinked cotton of course has lower value of activation energy.

### Observation of fiber expansion

To confirm the loose structure of crosslinked cotton fabrics with DMDHEU-amino acids, the expansion patterns (SEM) of the cross section of the 3% DMDHEU-, DMDHEU-serine-, and DMDHEU-glycine-crosslinked fibers are shown in Figures 3(a), 3(b), and



**Figure 3** The expansion patterns (SEM,  $\times 4000$ ) of cross section of the 3% (a) DMDHEU-, (b) DMDHEU-serine-, and (c) DMDHEU-glycine-crosslinked fibers, separately.

3(c), separately. Generally, the uncrosslinked cotton fiber has almost full expansion and the higher crosslinked cotton fiber has little or no expansion.<sup>17</sup> The figures show that the degree of the expansion of the DMDHEU-crosslinked fiber is lower than that of the DMDHEU-amino acids-crosslinked fibers, and that of DMDHEU-serine is slightly higher than that of DMDHEU-glycine. Those results agree with the data of structural diffusion resistance constants for the various crosslinked cotton fabrics shown in Table I.

#### Agent distribution

The  $K/S$  and  $[D]_f$  values of the fabrics crosslinked with DMDHEU, DMDHEU-serine, and DMDHEU-glycine listed in Table II are found to be decreasing with the increasing of the concentration of crosslinking agents in padding bath. It is well known that the crosslinks of the crosslinked fabrics could resist the dye adsorption to reduce the amount of dye adsorbed in the fiber.<sup>10,12</sup> The relationships between  $K/S$  and  $[D]_f$  values are plotted in Figure 4, accord-

ing to the method described by Rowland et al.<sup>4-6</sup> The linear relationships are similar to their results.<sup>16</sup> Color intensity ( $K/S$ ) is an inverse measure of crosslinking on fabric surfaces, and dye content is an inverse measure of total crosslinking content through fabric thickness.  $K/S$  results are average for the two sides of the fabric samples.

For a negative staining condition, agent distribution follows the rule that the lower the value of  $K/S$  at a specific level of dye content and the lower the dye fixation on the surface of the fabric, the higher the concentration of crosslinks on the surface of the fabric and the greater the agent distribution on the fabric. Figure 4 reveals only slightly lower values of  $\log K/S$  for DMDHEU-amino acids-crosslinked fabrics than that for DMDHEU-crosslinked fabric at the same value of  $\log [D]_f$ , i.e., the surface distribution of crosslinking agent on the crosslinked fabrics for DMDHEU-amino acids is slightly higher than that for DMDHEU alone. The higher surface distribution for DMDHEU-amino acids may be caused by the higher condensation reaction between the *N*-methylol group of DMDHEU and the amino group of serine and glycine.

The view point of higher condensation between the hydroxyl group of DMDHEU and the amino group of amino acids (serine and glycine) from the surface distribution of agents and the higher expansion of cross section of the DMDHEU-serine and DMDHEU-glycine-crosslinked cotton fibers can meet the higher wet crease recovery angles of the DMDHEU-serine and DMDHEU-glycine crosslinked fabrics.<sup>2</sup>

## CONCLUSIONS

The amino acids of serine and glycine were used to combine with DMDHEU as crosslinking agents to

TABLE II  
The  $K/S$  and  $[D]_f$  Values of Cotton Fabrics Finished with DMDHEU Alone, DMDHEU-Serine, and DMDHEU-Glycine

Crosslinking agents	Agent Conc. (%)	$K/S$ values	$[D]_f$ (dye/kg cotton)
DMDHEU	2	13.25	12.92
	4	3.76	2.94
	6	2.37	1.76
	8	2.04	1.49
DMDHEU-serine (mole ratio 3:1)	2	13.17	15.62
	4	5.28	5.67
	6	3.51	3.34
DMDHEU-glycine (mole ratio 3:1)	8	3.03	2.34
	2	14.72	16.53
	4	5.95	6.28
	6	4.38	3.85
	8	3.11	2.64

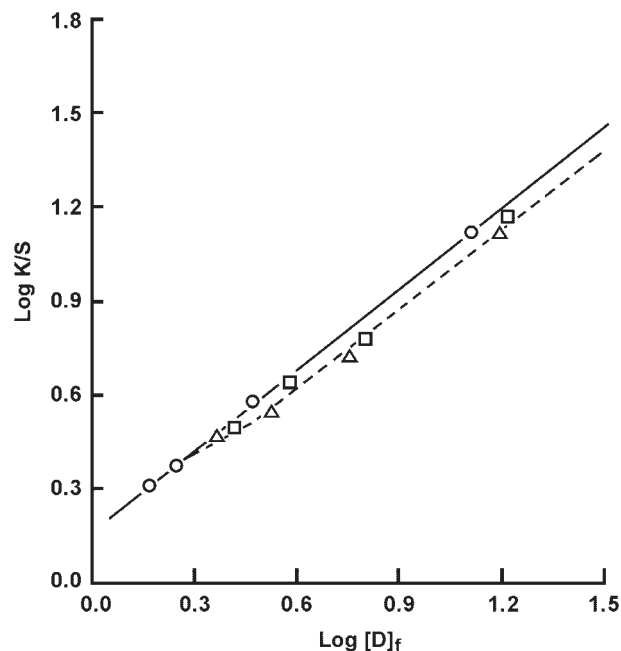


Figure 4 Plots of  $\log K/S$  versus  $\log [D]_f$  for fabric samples crosslinked with (○) DMDHEU, (△) DMDHEU-serine, and (□) DMDHEU-glycine, separately.

study the pore structure of the crosslinked cotton fabrics in this study. We found that the values of the dye absorption and rate constant for the various crosslinking agents are in the rank of DMDHEU-glycine > DMDHEU-serine > DMDHEU alone at a same dyeing temperature and time interval. The equilibrium absorption values for the DMDHEU-serine and DMDHEU-glycine crosslinked fabrics are higher than that for DMDHEU alone at a given temperature. Additionally, the equilibrium absorption value for DMDHEU-glycine-crosslinked cellulose is higher than that for DMDHEU-serine. Structural diffusion resistance constants for the three crosslinked fabrics that were dyed with direct dye and at a same dyeing temperature show the rank of DMDHEU-serine > DMDHEU-glycine > DMDHEU. The activation energies for the three crosslinked fabrics are ranked as follows: DMDHEU > DMDHEU-glycine > DMDHEU-serine. The expansion patterns (SEM) of cross section show that the degree of the expansion of the DMDHEU-crosslinked fiber is lower than that of the DMDHEU-amino acids-crosslinked fibers, and that of DMDHEU-serine is slightly higher than that of DMDHEU-glycine. The surface distribution of crosslinking agent on the crosslinked fabrics for DMDHEU-amino acids is slightly higher than that for DMDHEU alone. We suggest that the coreactant amino acids crosslinked fabrics have larger pore structure and slightly higher degree of surface distribution.

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