Diffusion Properties of Reactive Dyes into Net Modified Cotton Cellulose with Triazine Derivative

Kongliang Xie,[1] Yan Sun,[1] Aiqin Hou[2]

[1]*Modern Textile Institute, Donghua University, Shanghai 200051, China*
[2]*National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 200051, China*

Received 22 February 2006; accepted 15 May 2006
DOI 10.1002/app.25097
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cotton fabric is chemically modified with a 1,3,5-triazine derivative containing multireactive and multicationic groups. The diffusion properties of the reactive dyes into net modified cotton cellulose are investigated. When the dyeing temperature is raised, the dye uptake increases gradually and approaches equilibrium after dyeing for 60 min. The diffusion coefficients at different temperatures and the activation energy of the dye are discussed. Compared with unmodified cellulose, the diffusion kinetics of the dye in the net modified cotton cellulose show significant changes. The activation energies of dyes in net modified cotton fibers are much lower than those of dyes in unmodified cotton. The dyeing behavior of the modified cotton is analyzed and compared with the unmodified cotton. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2166–2171, 2007

Key words: modification; diffusion coefficients; activation energies

INTRODUCTION

It is one of important methods to modify cotton fabric with chemical graft in order to improve the dyeing property and reduce wastewater pollution.[1–4] Cellulose fiber dye systems pose environmental questions because of their high salt requirement and colored effluent discharge. The wastewater problem is therefore one of the most urgent issues in the textile finishing industry. In order to reduce the use of salt and increase dye bath exhaustion, a number of attempts have been made to modify cotton fibers using compounds containing certain groups. In our recent research work, net modified cotton fabric with a 1,3,5-triazine derivative containing multireactive and multicationic groups, 2,4,6-tri[(2-hydroxy-3-trimethylammonium) propyl]-1,3,5-triazine chloride (Tri-HTAC), was investigated. As expected, the physical and mechanical properties of net modified cotton fiber are quite different from those of conventional cotton fabric, and this is particularly true of their dyeing characteristics. Compared with unmodified cellulose, the net modified cotton cellulose exhibits different behavior toward dyeing. The color yield was higher than that on untreated cotton, despite the addition of large amounts of salt in the latter case. The modified cotton had better wash fastness than the untreated cotton. This will be of great benefit, because it will enable a reduction in the salt present in dye house effluent.

The present article advances the knowledge of the diffusion properties of reactive dyes into net modified cotton cellulose with a triazine derivative containing multireactive groups. Reactive Red BF-3B and Reactive Blue BF-RN were used. Their dyeing kinetics in net modified cotton were studied, and the diffusion coefficients and activation energies of the dyeing were calculated.

EXPERIMENTAL

Materials

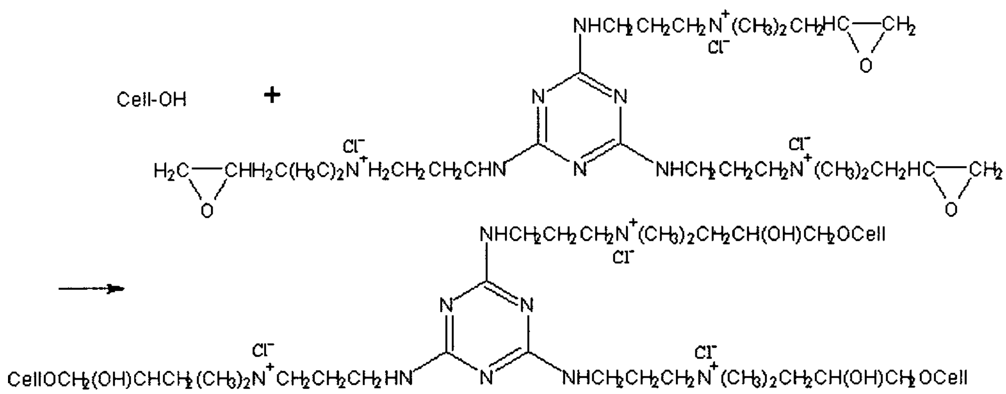
Desized, scoured, and bleached cotton fabrics were obtained from Beijing Textile Company. Reactive Red BF-3B and Reactive Blue BF-RN were obtained from Shanghai Matex Chemical Company and used without further purification.

Net modifying to cotton fabric

Tri-HTAC was dissolved in distilled water to give solutions at 10% concentration by weight. To the solution was added 1.5% sodium hydroxide as a catalyst. Samples of cotton were padded with the solutions to give 100% wet pick-up, placed in plastic sample bags, tightly sealed to prevent air penetration, and kept at room temperature for 4 h. The treated fabrics were then washed with tap water until neutral and again washed in warm water using

Correspondence to: K. Xie (klxie@dhu.edu.cn).

Journal of Applied Polymer Science, Vol. 103, 2166–2171 (2007)



Scheme 1 The structure of net modified cotton.

a domestic washing machine to remove unfixed Tri-HTAC. The fabric was air dried at room temperature.

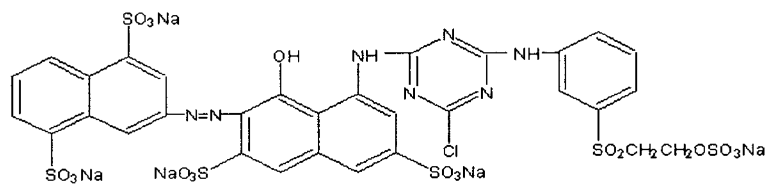
Dyeing of treated and untreated cotton fabric

The unmodified and modified cotton fabrics were dyed in an IR dyeing machine (PYROTEC-2000) with a dye concentration of 2 g/L and a liquor ratio of 1 : 500 at pH 7. The fabrics were removed from the machine after dyeing, rinsed thoroughly in hot tap water until the rinsing water was clear, and air dried. To determine the apparent activation energies, isotherms were carried out at 25, 35, 45, and 65°C on the unmodified and modified cotton fabrics. The dye absorption at each time was determined using a Shanghai 723 spectrophotometer. The K/S values of dyed samples were determined using a Datacolor Spectraflash SF600 Computer Color-Matching System in order to monitor the dye bath concentration. The dye uptake on dyed samples was calculated through standard curves of the K/S values.

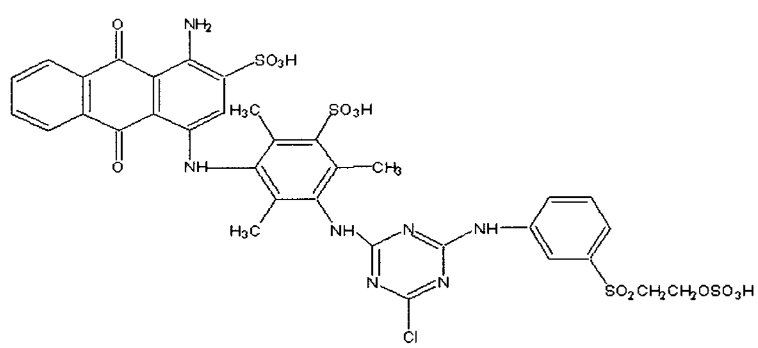
RESULTS AND DISCUSSION

Influences of temperature and dyeing time

After the cotton fabric is chemically modified with Tri-HTAC, a 1,3,5-triazine derivative containing mul-



Reactive Red BF-3B



Reactive Blue BF-GN

Scheme 2 The structures of Reactive Red BF-3B and Reactive Blue BF-RN dyes.

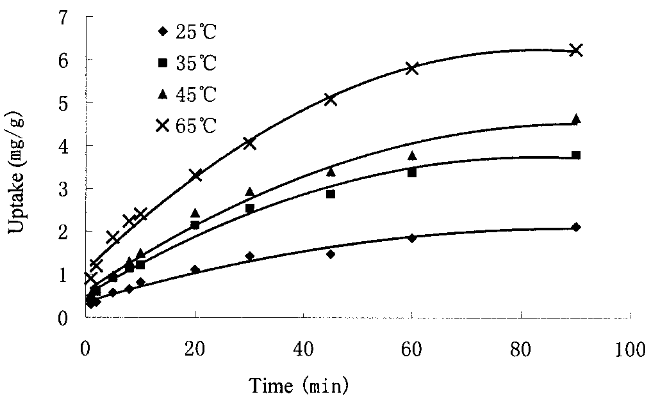


Figure 1 The effects of the dyeing time and temperature on the dye uptake of unmodified cotton with Reactive Red BF-3B.

tireactive and multicationic groups, the chemical and morphological structure of the net modified cotton cellulose can change. Compared with unmodified cellulose, the net modified cotton cellulose exhibits different behavior toward dyeing because of the presence of numerous quaternary ammonium groups on the net modified cotton (Scheme 1).

The dyes used in the study were Reactive Red BF-3B and Reactive Blue BF-RN (see Scheme 2). Figures 1, 2, 3, and 4 show the influences of the temperature and dyeing time on the dye uptake on unmodified cotton and net modified cotton at 25, 35, 45, and 65°C, respectively.

The results show that the dye uptake increased initially with the dyeing time, then it slowed down after 50 min and reached equilibrium after 60 min. The dyeing temperature had a strong influence on the dye uptake. The higher the temperature was, the more the dye sorbed by the fiber. Figures 1 and 2 were compared with Figures 3 and 4, respectively. It is clear that the dye uptakes were higher on the modified cotton than those on unmodified cotton at any time with both dyes. This conclusion is valid for

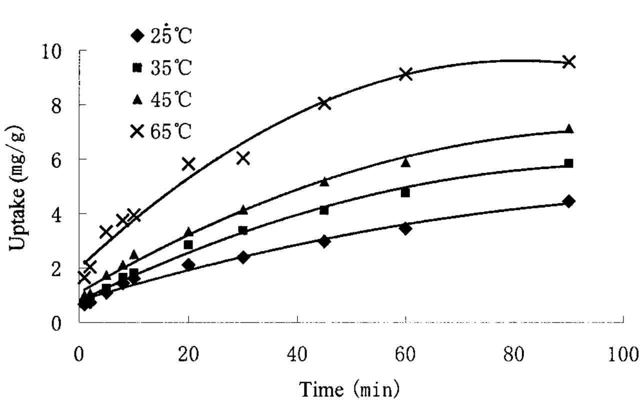


Figure 2 The effects of the dyeing time and temperature on the dye uptake of unmodified cotton with Reactive Blue BF-RN.

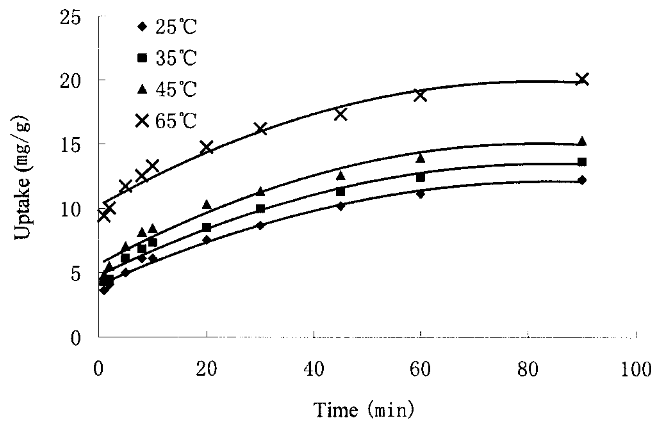


Figure 3 The effects of the dyeing time and temperature on the dye uptake of net modified cotton with Reactive Red BF-3B.

each dye bath temperature and can be explained by the larger quaternary ammonium groups on the net modified cotton exposed to the dye molecules than that for unmodified cotton.

Diffusion rate constants

The transfer of a dye molecule from the dye solution into a fiber is usually considered to involve the initial mass transfer from the bulk solution to the fiber surface and adsorption of the dye on the surface, followed by diffusion of the dye into the fiber.[5] The diffusion of the dye within the fiber is rate controlling. The diffusion in a fabric is much more difficult than in solution because of dye–fiber interactions and mechanical obstruction by the fiber molecules in the pores. Diffusion of dyes into fibers during dyeing can take place under either finite or infinite dye bath conditions. This is never strictly true, but it reflects the mathematical assumptions made in modeling the dyeing process. In an infinite dye bath, the dye concentra-

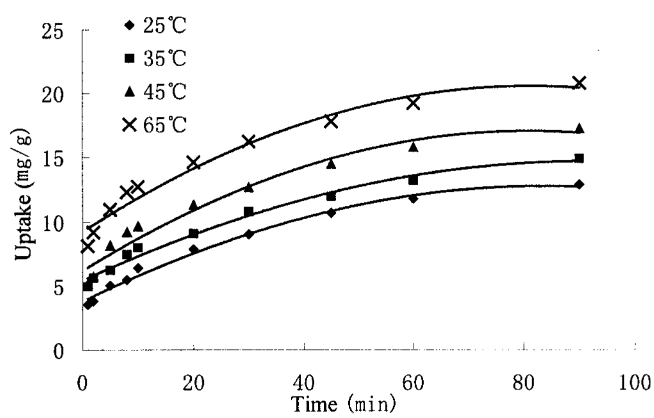


Figure 4 The effects of the dyeing time and temperature on the dye uptake of net modified cotton with Reactive Blue BF-RN.

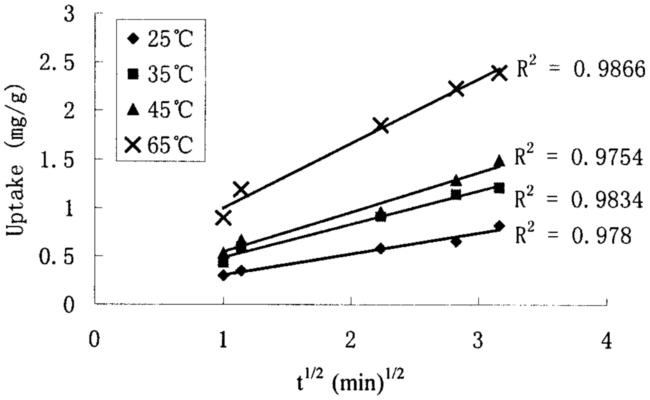


Figure 5 The dye uptakes on unmodified cotton versus the square root of the dyeing time with Reactive Red BF-3B.

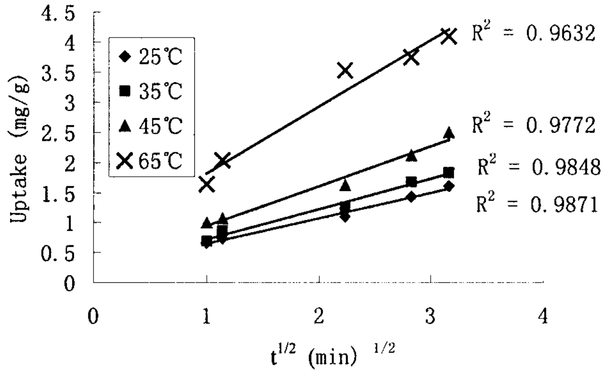


Figure 7 The dye uptakes on unmodified cotton versus the square root of the dyeing time with Reactive Blue BF-RN.

tion does not change during the sorption process. In a finite dye bath, the dye concentration at the fiber surface continuously decreases during the sorption process. If the initial dye concentration is high, infinite dye bath conditions are maintained throughout the dyeing process. In the present work the diffusion coefficient is analyzed for the infinite dye bath condition.

The Fickian equations describe the diffusion of a dye within a fiber. Solutions to dyeing diffusion equations are mathematically complex and experimental studies are difficult. The differential equations applied to real dyeing situations with fibers usually require appropriate assumptions leading to an approximate solution. One simplification is to assume that the external dye bath has a constant concentration. This gives what is known as steady-state diffusion. Another simplification is based on the conditions at the beginning of the dyeing process. The amount of dyes in the fiber at any time is directly related to the square root of the dyeing time (t), as shown in eqs. (1) and (2).[5]

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial r^2} + \frac{z}{r}\left(\frac{\partial c}{\partial t}\right)\right\} \tag{1}$$

$$\frac{C_t}{C_\infty} = 2\sqrt{\frac{D_f t}{\pi}} \tag{2}$$

where C_t represents the dye concentration in the fiber at t and C_∞ represents the dye concentration in the fiber at equilibrium. At a certain temperature, the value of C_∞ is constant.

This gives eq. (3)[6]

$$C_t = Dt^{1/2} \tag{3}$$

where D is the diffusion coefficient.

Figures 5, 6, 7, and 8 show the dye uptakes versus the square root of t at 25, 35, 45, and 65°, respectively, on unmodified cotton and net modified cotton. The diffusion coefficients (shown in Table I) at different temperatures were evaluated from the slopes of the corresponding linear plots. It can be seen that the diffusion coefficient increased as the temperature rose. The results show that the values of the diffusion coefficient were 3–7 times higher for net modified cotton than those for unmodified cotton. The absorption rates of dyes on net modified cotton were significantly improved.

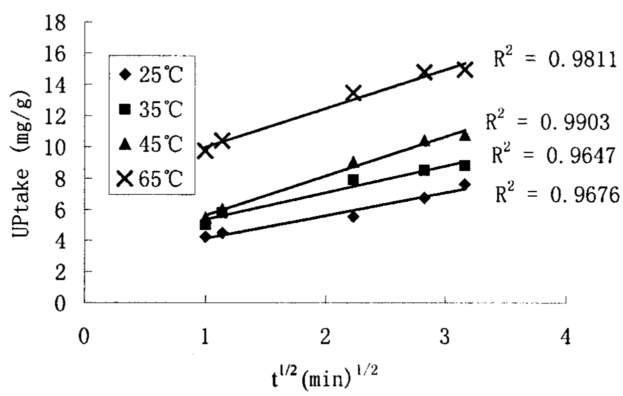


Figure 6 The dye uptakes on net modified cotton versus the square root of the dyeing time with Reactive Red BF-3B.

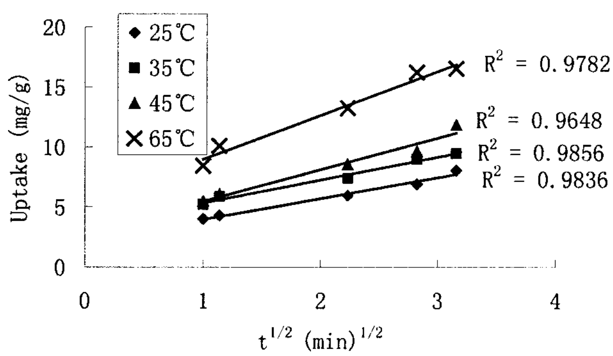


Figure 8 The dye uptakes on net modified cotton versus the square root of the dyeing time with Reactive Blue BF-RN.

TABLE I
Diffusion Coefficients (*D*) of Dyes at Different Temperatures

	D			
	Unmodified cotton		Net modified cotton	
Temperature (°C)	BF-3B	BF-RN	BF-3B	BF-RN
25	0.2184	0.4279	1.4728	1.7456
35	0.3445	0.5073	1.7150	1.9124
45	0.4107	0.6621	2.5229	2.6451
65	0.6620	1.1037	2.4883	3.6718

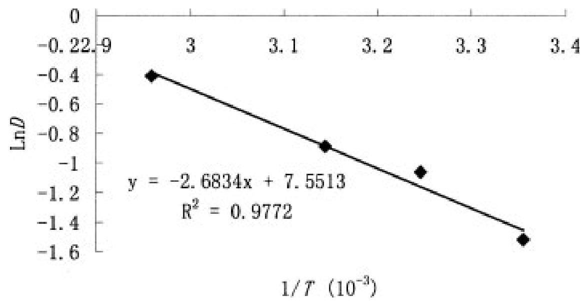


Figure 9 The relationship between ln *D* and $1/T$ on unmodified cotton with Reactive Red BF-3B.

Apparent activation energies

The effects of temperature changes are normally expressed in terms of the activation energy of the process. The apparent activation energies have been determined from the diffusion coefficient at different temperatures. For this purpose, the changes in the diffusion coefficient are described by the Arrhenius equations [eqs. (4), (5)].[7]

$$D = D_0 e^{-(E/RT)} \tag{4}$$

$$\ln D = -\frac{E}{RT} + \ln D_0 \tag{5}$$

where E is the activation energy, D_0 is a constant independent of the temperature, R is the universal gas

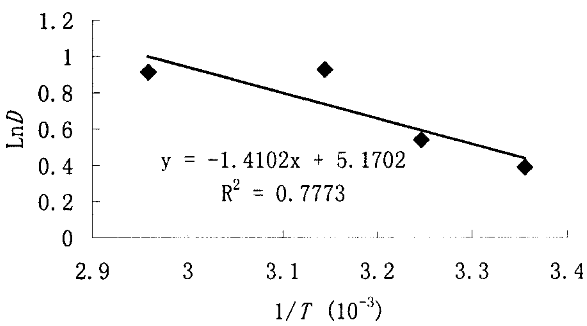


Figure 10 The relationship between ln *D* and $1/T$ on net modified cotton with Reactive Red BF-3B.

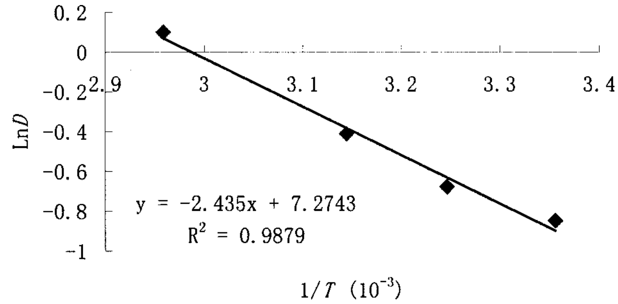


Figure 11 The relationship between ln *D* and $1/T$ on unmodified cotton with Reactive Blue BF-RN.

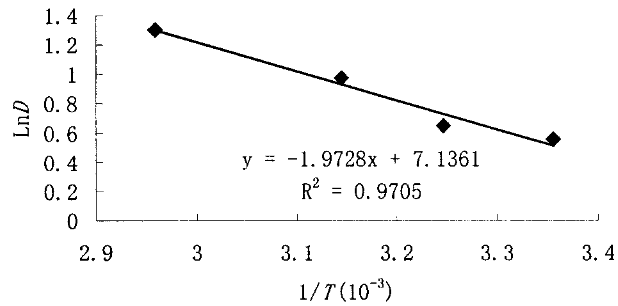


Figure 12 The relationship between ln *D* and $1/T$ on net modified cotton with Reactive Blue BF-RN.

constant, and T is the temperature. The value of E is found from the slope of the graph of ln *D* versus $1/T$.

The relationship between ln *D* and $1/T$ presented a line (see Figs. 9–12), and the activation energy for the dye diffusion in the fibers could thus be calculated (see Table II).

The activation energy is the energy that the dye molecule must overcome in order to be able to move, and it can be regarded as a measure of a barrier to movement of dye. The results in Table II show that the activation energies of net modified cotton were lower than those of unmodified cotton. The difference between them indicated that the barrier to movement of the dye in net modified cotton fibers was much lower than that of the dye in unmodified cotton. There were more sites in the net modified cotton that were capable of attracting the dye. Moreover, the net modified cotton was more intensely dyed in its interior than unmodified cotton.

TABLE II
Activation Energies of Unmodified and Net Modified Cotton with Reactive Red BF-3B and Reactive Blue BF-RN

	E (kJ/mol)	
	BF-3B	BF-RN
Unmodified cotton	22.31	20.24
Net modified cotton	11.72	16.45

CONCLUSION

Cotton fabric was chemically modified with a 1,3,5-triazine derivative containing multireactive and multicationic groups (Tri-HTAC). The dye uptake approached equilibrium after dyeing for 60 min. Compared with unmodified cotton, the diffusion coefficients in the net modified cotton were higher. The activation energies of net modified cotton were lower than those of unmodified cotton. The difference between them indicated that the barrier to movement of the dyes in net modified cotton fibers was much lower than that of the dye in unmodified cotton.

References

1. Lim, S.-H.; Hudson, S. M. Color Technol 2004, 120, 108.
2. Kamel, M. B.; Youssef, H.; Shokry, G. M. J Soc Dyers Colorists 1996, 114, 101.
3. Baker, D. A.; East, G. C.; Mukhopadhyay, S. K. J Appl Polym Sci 2001, 79, 1092.
4. Wang, H.; Lewis, D. M. Color Technol 2002, 118, 159.
5. Broadbent, A. D. Basic Principles of Textile Coloration; Society of Dyers and Colourists: West Yorkshire, U.K., 2001; p 209.
6. Patterson, D.; Sheldon, R. P. Trans Faraday Soc 1959, 55, 1254.
7. Peters, R. H. Textile Chemistry; Elsevier Scientific: New York, 1975; Vol. III, p 177.