Kinetics of Swelling of Cotton Fibers in Aqueous Ethylenediamine Solutions Using Moisture Regain Data

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Synopsis

Kinetic studies of swelling of cotton cellulose with 75% (w/w) EDA solution have been carried out. Three rates of the reaction were observed in the temperature range 10–35°C: first, the very fast rate (k_1) lasting for about 10 s; second, the extremely slow rate (k_2) lasting for 30–50 s; and third, once again a fast rate (k_3), k_1 being faster than k_3. k_1 was attributed to the swelling action of EDA–monohydrate in amorphous regions of cellulose; k_2 was assigned to the penetration of swelling species into crystallites accompanied by breakage of H bonds in these regions; and k_3 was assigned to the opening up of the crystallites. Activation energy values confirmed this trend. At higher temperatures (35–55°C), the middle rate k_2 merged with k_3, giving only two rates, k_1 and k_{2+3}, as the higher temperatures brought about simultaneous diffusion of swelling agent into, and decrystallization of, the crystalline portions of cellulose. EDA solution of 65% (w/w) concentration gave only two rates: the initial fast rate assigned to the swelling of the amorphous portion, followed by a slow one, operating in mesomorphous regions of cellulose, without any appreciable decrystallization. This was attributed to the important fact, viz., the absence of EDA–monohydrates in the solution.

INTRODUCTION

Kinetic studies of swelling reactions are important from the point of view of understanding mode of swelling and decrystallization of fibers. These studies are also helpful in investigating the internal structure of polymeric substances.

Newns[1–5] observed two distinct stages of sorption/desorption kinetics of the cellulose/water system, which were explained in terms of the diffusion–relaxation mechanism. Although a considerable amount of work has been reported in the literature on the swelling of cotton in diamines, hardly any data have been published on the kinetics of the swelling reaction of cellulose with ethylenediamine due to, perhaps, the very rapid rate of the swelling reactions.[6,7]

The present paper reports results of kinetic studies on the swelling reaction on cotton cellulose with ethylenediamine through measurement of accessibility to water vapor.

EXPERIMENTAL

Materials

Good quality long staple Sudanese cotton in loose form was used after puri-

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fication using a standard procedure.[8] The purification of fibers essentially involved scouring and bleaching under specified conditions. Ethylenediamine was of CP grade. It was distilled twice before use.

Preparation of Swollen Cotton Samples

The purified cotton cellulose was treated with 75% and 65% (w/w) aqueous ethylenediamine solutions at 10°C, 20°C, 35°C, 45°C and 55°C for different lengths of time. At the end of treatment, samples were washed with water at the respective temperatures of treatment followed by thorough washing with tap water. Swollen samples were then squeezed and kept in distilled water at 30°C for about 1 h. Finally they were washed with distilled water twice to ensure removal of traces of ethylenediamine. The samples were then air-dried and conditioned at 75% RH and 30°C.

Determination of Moisture Regain and Accessibility

Moisture regain of swollen samples was determined under conditions of adsorption. The swollen samples were kept over phosphorus pentoxide in a desiccator for about 4 h to reduce the moisture content of the samples below the regain value and then conditioned at 75% RH at 30°C ± 1°C for 72 h. About 1 g of the conditioned sample was weighed accurately and dried in an electric oven at 110°C ± 1°C to constant weight. Percentage of moisture regain was calculated on the basis of oven-dry sample weight. The amorphous fraction present in the fiber substance was calculated using Valentine's formula.[9] The residual mass of the fiber was taken as the crystalline portion.

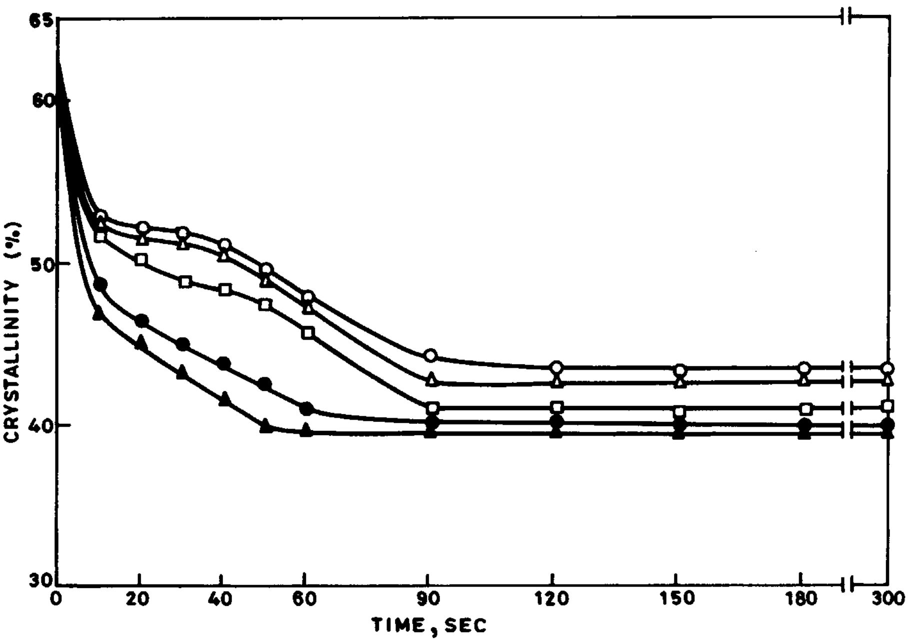

Fig. 1. Crystallinity vs. time of swelling reaction of cotton fibers with 75% (w/w) EDA: (○) 10°C; (△) 20°C; (□) 35°C; (●) 45°C; (▲) 55°C.

RESULTS AND DISCUSSION

The results of the present investigation indicate that, with increase in time of swelling treatments, moisture regain of the swollen samples goes on increasing progressively and so also the accessibility, while the crystalline fraction is correspondingly decreased. These results with respect to EDA solution of 75% (w/w) are plotted in Figure 1. Effect of rise in temperature from 10°C to 55°C indicates that the accessibility increases with rise in temperature of the treatment at a given time of swelling reaction. Longer times of treatment at a given temperature facilitate penetration of the EDA–H_2O monohydrate into deeper regions of the semicrystalline and crystalline regions of cellulose, while higher temperatures of treatment enhance the EDA–H_2O monohydrate capacity to interact with cellulose, in addition to bringing about greater vibrations of cellulose chains as a result of higher levels of thermal energy at the elevated temperatures.

In order to study the kinetic behavior of the swelling and decrystallizing reactions, a logarithmic plot of crystallinity vs. time of swelling reaction was plotted

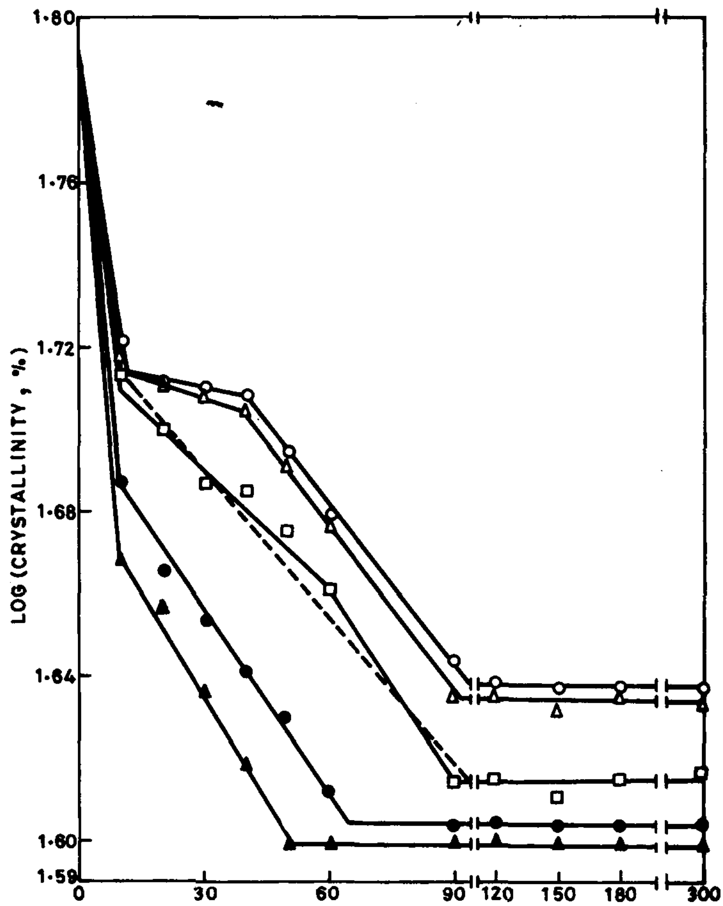

Fig. 2. Rate curves for swelling reaction of cotton fibers with 75% (w/w) EDA: (○) 10°C; (△) 20°C; (□) 35°C; (●) 45°C; (▲) 55°C.

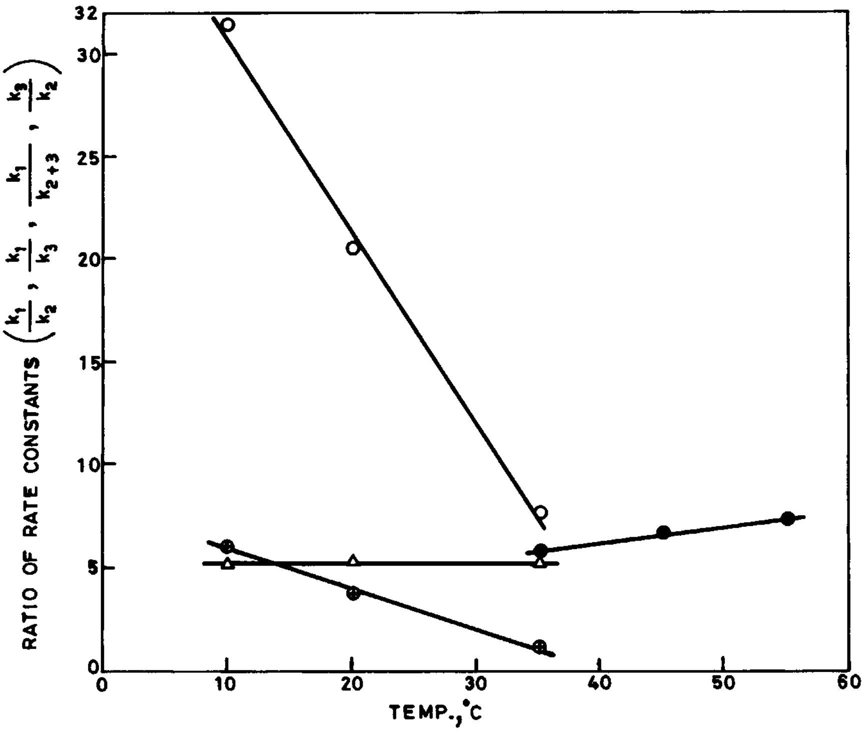

Fig. 3. Ratio of rate constants vs. temperature for 75% (w/w) EDA: (○) k_1/k_2; (△) k_1/k_3; (●) k_1/k_{2+3}; (⊕) k_3/k_2.

(Fig. 2). It can be seen, in general, that the swelling reaction proceeds for a certain definite duration of time which is a function of the temperature of treatment. Beyond this, there appears a leveling-off effect with almost zero change in crystallinity. The duration of change depends upon the temperature of treatment, the longest of 90 s being at the lowest temperature, say 10°C, and vice versa, i.e., 50 s at 55°C. It can be seen that at 10°C, 20°C, and 35°C there are three rates, the initial very fast rate (k_1) followed by the extremely slow rate (k_2) from about 10 to 40 s and finally a slower rate (k_3). It is significant to note that k_2 becomes faster and faster with progressive reduction in duration of time when the temperature is raised from 10°C to 35°C and finally merges in k_3 at 45°C and above. Thus, at 45°C and 55°C, only two rates are observed, the initial fast one k_1 followed by a slower one, which is, in effect, the combination of k_2 and k_3, designated as k_{2+3}. It can be seen that the reaction follows the first-order kinetics. The temperature of 35°C seems to be a transitional one and hence, for all practical purposes, can be grouped either with the two lower temperatures of 10°C and 20°C or with the higher two temperatures of 45°C and 55°C.

As regards k_1, it increases with rise in temperature of treatment from 10°C to 55°C. k_1, therefore, may be assigned to the swelling phenomenon taking place mainly in the amorphous and mesomorphous regions of cotton cellulose. The intermediate rate k_2 lasts for a much longer time as compared to the fast rate k_1. k_2 is, therefore, assigned to the penetration of the EDA–monohydrate into

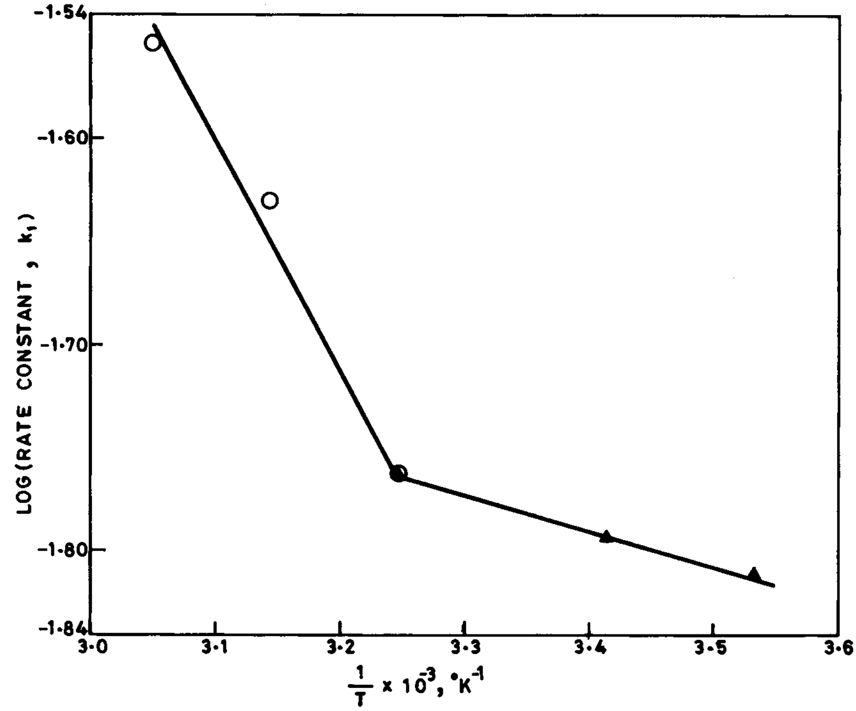

Fig. 4. Activation energy E_1 of swelling reaction in 75% (w/w) EDA: (▲) E_1 (10–35°C); (O) E_1 (35–55°C).

the crystallites and, that is why the values of k_2 are lower at lower temperatures. k_3 is assigned to the reaction of actual decrystallization through the breakage of H bonds in the penetrated crystalline portions, and, hence, its value goes on increasing with the increase in temperature from 10°C to 35°C. At 35°C and above, the penetration of the swelling species and the breakage of the H bonds in the ordered regions are so powerful that these two reactions are almost simultaneous, and hence, k_2 and k_3 merge to give a combined reaction with a combined rate constant k_{2+3}. Obviously, the value of the rate constant k_{2+3} goes on increasing with the increase in temperature of swelling from 35°C to 55°C.

Table I gives the values of rate constants (k_1), (k_2), (k_3), and (k_{2+3}) and their ratios as well as the activation energy values (Fig. 3). The ratio k_1/k_2 decreases rapidly with the increase in temperature showing that k_2 is increased at a much faster rate than the increase in k_1 as a result of the rise in temperature of the swelling medium. This is obvious since the penetrating power and swelling efficiency of EDA–monohydrate are accelerated at higher temperatures. The results, therefore, suggest that at higher temperatures the rate of penetration increases with much faster rate than the increase in the rate of actual decrystallization. It is interesting to note that, unlike k_1/k_2, k_1/k_3 is independent of temperature, indicating that the swelling in the amorphous region and separation of chains in crystalline portions during decrystallization are affected proportionately, when the temperature is raised from 10°C to 35°C, the fact which speaks of the identical mechanism of swelling action of ethylenediamine–

TABLE I

Rate Constant and Activation Energy Values for Ethylenediamine[a]-Swollen Cotton Fibers[b]

Temp (°C)	Rate constant × 10^{-5} s^{-1}								Activation energy (kcal/mol)			
	k_1	k_2	k_3	k_{2+3}	k_1/k_2	k_1/k_3	k_1/k_{2+3}	k_3/k_2	E_1	E_2	E_3	E_{2+3}
10	1543.01	48.96	291.69	—	31.51	5.29	—	5.96				
20	1612.10	78.62	309.14	—	20.50	5.36	—	3.83	0.78	10.94	0.69	—
35	1727.25	224.27	322.42	308.02	7.71	5.36	5.61	1.44				
45	2349.06	—	—	345.45	—	—	6.80	—	5.07	—	—	1.84
55	2786.63	—	—	368.48	—	—	7.56	—				

[a] 75% (w/w) aqueous EDA, washing with water.

[b] From moisture regain data.

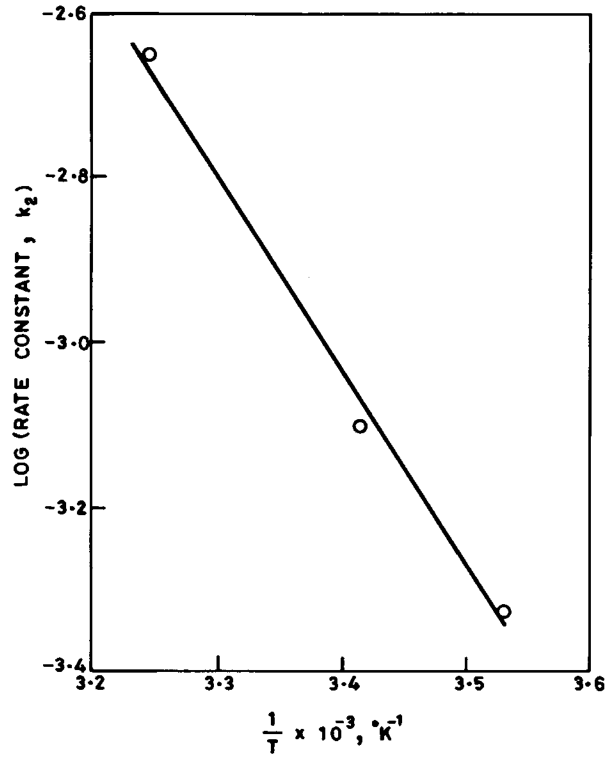

Fig. 5. Activation energy E_2 of swelling reaction in 75% (w/w) EDA.

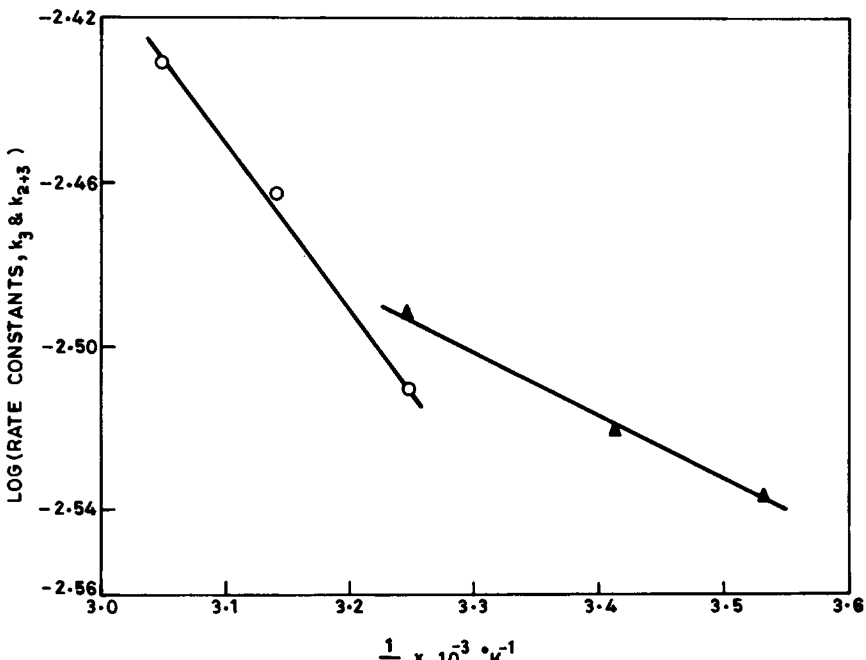

Fig. 6. Activation energies E_3 and E_{2+3} of swelling reaction in 75% (w/w) EDA: (▲) E_3 (10–35°C); (O) E_{2+3} (35–55°C).

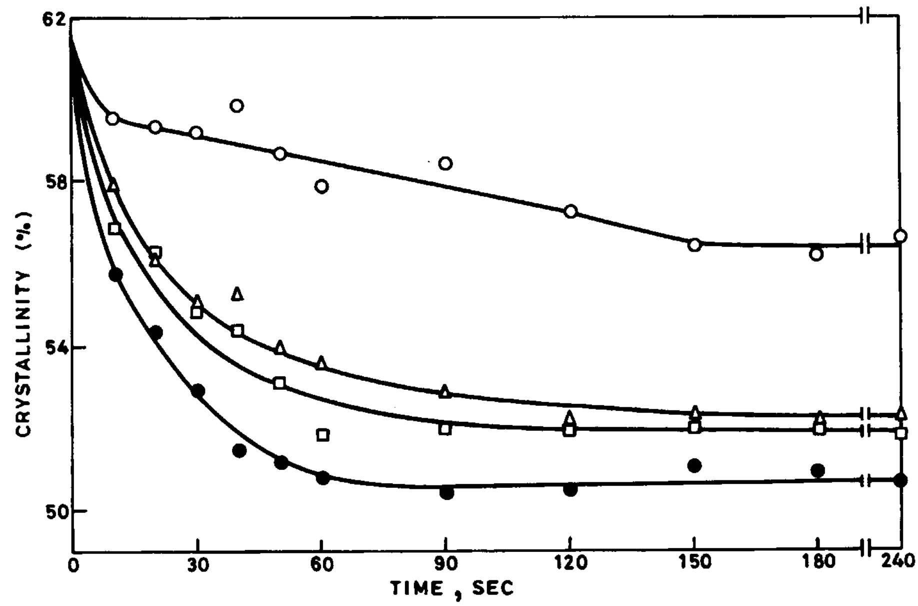

Fig. 7. Crystallinity vs. time of swelling reaction of cotton fibers with 65% (w/w) EDA: (○) 20°C; (△) 35°C; (□) 45°C; (●) 55°C.

monohydrate on the two respective regions of the fiber. It is also interesting to observe that k_1/k_{2+3}, unlike the k_1/k_3 ratio, is not independent of temperature but goes on increasing with the rise in temperature from 35°C to 55°C, since the rates of penetration and decrystallization put together are hampered to a lesser extent as compared to the opening up of the disordered region at higher temperatures.

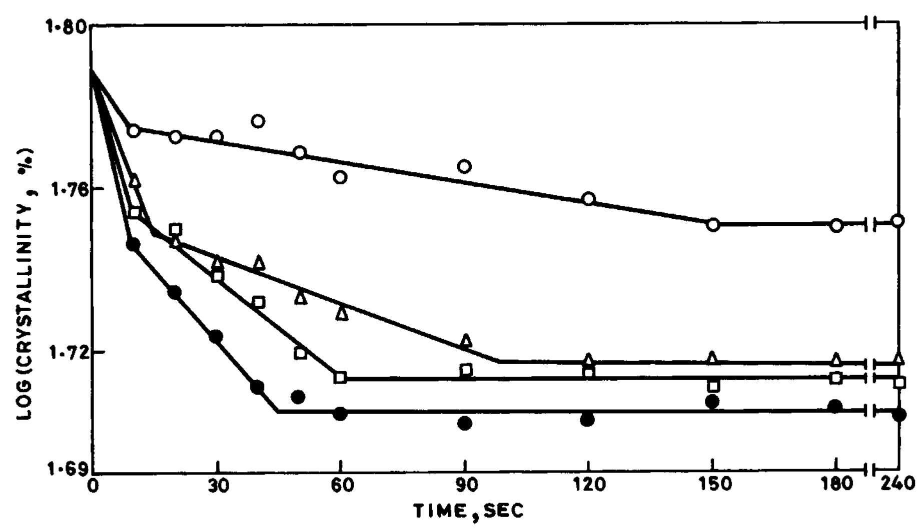

Fig. 8. Rate curves for swelling reaction of cotton fibers with 65% (w/w) EDA: (○) 20°C; (△) 35°C; (□) 45°C; (●) 55°C.

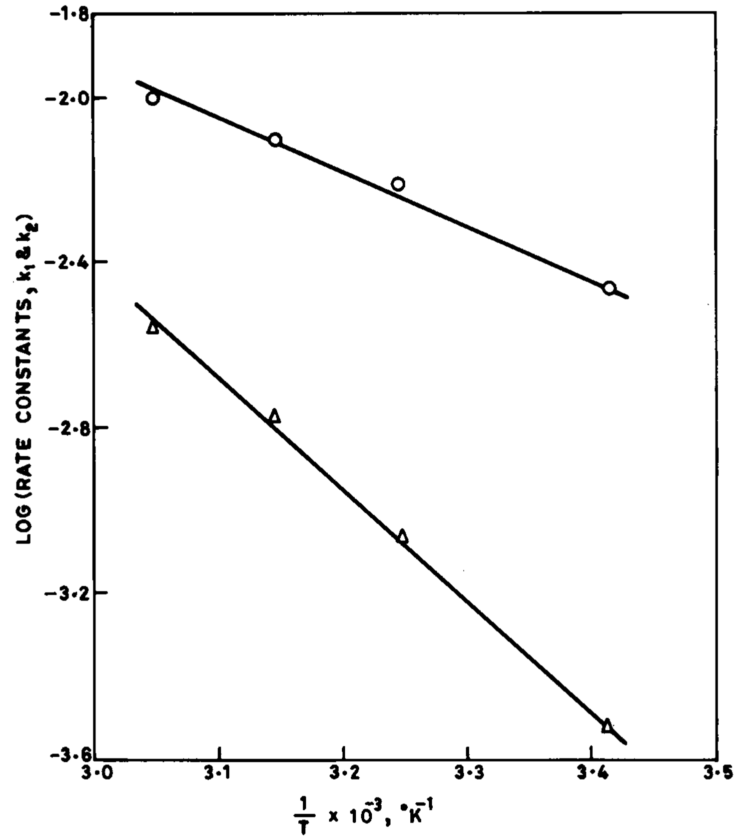

Fig. 9. Activation energies E_1 and E_2 of swelling reaction in 65% (w/) EDA: (○) E_1; (△) E_2.

The activation energy values E_1, E_2, and E_3 are 0.78, 10.94, and 0.70 kcal/mol, respectively (Figs. 4–6). E_1 and E_3 are quite comparable, confirming the earlier findings that these two are obtained by similar mechanism of swelling due to the EDA–monohydrate. E_2 has very high activation energy values, indicating that a considerable amount of energy has to be spent during penetration of the EDA molecules in highly ordered regions of cellulose.

The activation energy value for fast reaction, i.e., E_1 in the temperature range 35–55°C is 5.07 kcal/mol as against the corresponding value of only 0.78 kcal/mol for E_1 representing the temperature range 10–35°C. This indicates that at elevated temperatures the fast reaction is not restricted only to the truly amorphous portions but is also accompanied by the simultaneous penetration of the swelling species into the crystallites followed by at least some amount of decrystallization of the same. The E_{2+3} value is of the order of 1.84 kca/mol, indicating the ease of penetration and decrystallization reactions at higher temperatures. This may be due to the fact that part of these reactions are initiated much earlier, falling in the region of the fast reaction, partly because the swelling species are powerful enough to penetrate further into the ordered regions easily and simultaneously separating the cellulosic chains apart by breaking H bonds also with a relative ease.

The results with respect to swelling treatment of cotton fibers in 65% (w/w)

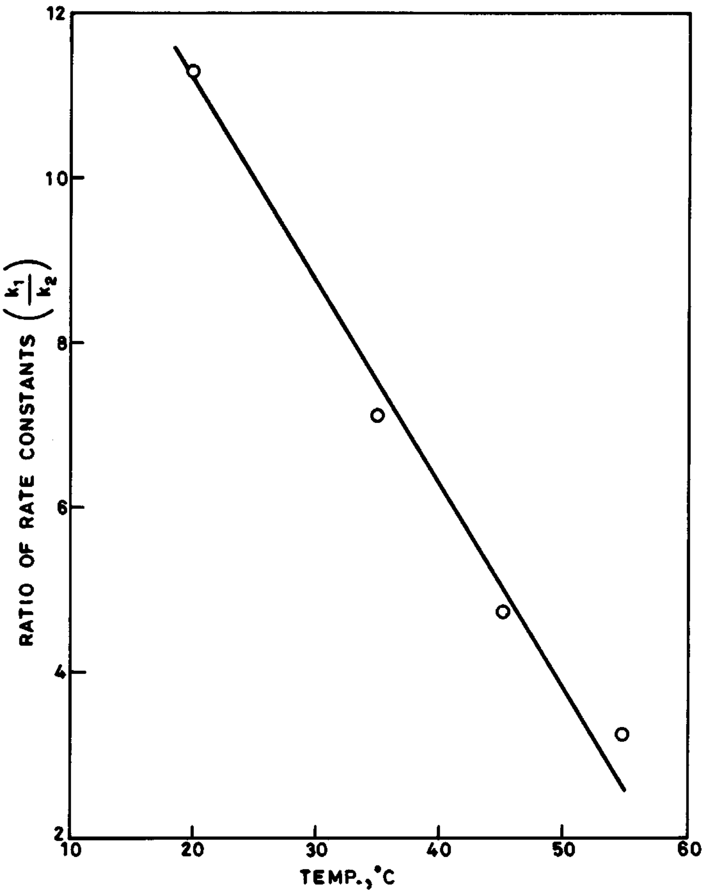

Fig. 10. k_1/k_2 vs. temperature for 65% (w/w) EDA.

aqueous EDA solution at different temperatures for varying lengths of time are plotted in Figures 7–10, while the data on kinetic studies of swelling are given in Table II. The results indicate that the trend is the same as in case of 75% (w/w) aqueous EDA solution except that (1) at 10°C the solution is ineffective, (2) the improvement in moisture regain capacity is lower, and (3) the middle slow rate is absent and only k_1 and k_2 are observed. This may be attributed to the absence

TABLE II
Rate Constant and Activation Energy Values for Ethylenediamine[a]-Swollen Cotton Fibers[b]

Temp (°C)	Rate constant × $10^{-5} \cdot s^{-1}$			Activation energy (kcal/mol)	
	k_1	k_2	k_1/k_2	E_1	E_2
20	345.45	30.69	11.25		
35	621.80	87.51	7.10	6.22	12.90
45	806.05	170.79	4.72		
55	909.29	276.36	3.29		

[a] 65% (w/w) aqueous EDA, washing with water.
[b] From moisture regain data.

of powerful ethylenediamine–monohydrate at 65% (w/w) concentration of EDA. The total fall in crystallinity is hardly 10% under the most severe conditions of treatment. This shows the lower effectiveness of 65% (w/w) concentration as compared to 75% (w/w) concentration of EDA. Further, the 65% (w/w) EDA seems to be incapable of penetrating the highly ordered regions. The two rates k_1 and k_2 are attributed to the opening up of the accessible portion of the fibers and opening up of the mesomorphous regions as well as surface of crystallites respectively. This is supported by the fact that E_2 (12.90 kca/mol) is greater than E_1 (6.22 (kcal/mol) since the 65% (w/w) EDA solution has to overcome the barrier of the mesomorphous region and simultaneously open up the structure. Penetration of the swelling agent in mesomorphous regions is helped at higher temperatures, which is reflected in the steady decrease in k_1/k_2 with increase in temperature of the swelling reaction.

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