Swelling Behavior of Cotton Fibers in Benzylamine and 4-Amino Acetophenone

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Synopsis

Swelling and decrystallizing action of aqueous solutions of benzylamine and mixtures of 4-amino acetophenone with methanol was studied on cotton fibers. The extent and type of swelling were studied by determining various characteristics of the swollen cotton, viz., moisture regain, acetyl number, infrared crystallinity index, and water of imbibition values. Benzylamine was found to be an intracrystalline swelling agent, while 4-amino acetophenone brought about changes in the accessible regions only. Benzylamine has been regarded as substituted methylamine, and its swelling and decrystallizing action on cotton fibers has been explained on the basis of its ability to form specific hydrates with water. The intercrystalline swelling action of 4-amino acetophenone resulted in further opening up of the accessible portions of the fiber. This was explained on the basis of its inability to form any specific complexes with methanol as well as its low basicity. The weak basic character of 4-amino acetophenone was attributed to the substitution of deactivating and *meta*-directing acetyl group in the *para*-position to the amino group of aniline.

INTRODUCTION

Swelling action of a number of organic and inorganic swelling agents on cellulosic fibers has been investigated extensively. Among the organic swelling agents, a number of workers studied the swelling reaction on cotton fibers using monoamines and diamines mostly from the aliphatic series.[1–3] Earlier, the unique swelling behavior of morpholine and its synergestic influence on swelling and decrystallizing action of ethylenediamine on cotton cellulose have been reported from these laboratories.[4–6] It was shown that the solubility parameter (δ) may not fully indicate the swelling ability of a reagent. It was further shown that, although morpholine and piperidine have almost identical solubility parameters, morpholine was found to be a very powerful swelling agent for cellulose, since it possesses a higher value of ($\delta H + \delta p$) as compared to the corresponding figure of the said parameters for piperidine, which had a very negligible swelling effect on cotton. A literature survey indicates that, although a considerable amount of work has been reported on the swelling action of a number of aliphatic monoamines on cellulose, there is no work published, so far, on the heterocyclic monoamines, such as benzylamine or 4-amino acetophenone, in which the amino nitrogen is outside the heterocyclic ring.

The present investigation reports the swelling reaction of aqueous benzylamine solutions as well as of 4-amino acetophenone of different concentrations in methanol, with cotton fibers.

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EXPERIMENTAL

Materials

Cotton Cellulose. Good quality, long-staple Sudanese cotton in loose form was used for swelling reaction after standard purification. The purified cotton cellulose had a DP of 2250, a copper number of 0.01, and a carboxyl content of 0.335 meq/100 g cotton.

Chemicals. All the chemicals including benzylamine and 4-amino acetophenone were of CP grade. The KBr used in the preparation of pellets for infrared spectroscopy was of Analar grade.

Methods

Preparation of Swollen Cotton Fibers. Purified cotton cellulose was treated with aqueous solutions of benzylamine at different concentrations between 10% and 100% at 20°C and 35°C for 1 h. At the end of the treatment, the samples were washed thoroughly with distilled water. The loosely held water was removed by suction. Samples were finally air-dried and conditioned at 75% RH and 30°C.

Similarly, swelling of cotton cellulose was carried out in methanol solutions of 4-amino acetophenone at different concentrations (5–25% at 20°C and 5–30% at 35°C) for 1 h. At the end of the treatment, the samples were repeatedly washed with methanol. The samples were rinsed with distilled water and the loosely held water was removed by suction. Samples were finally air-dried and conditioned at 75% RH and 30°C.

Conductivity Measurements. The conductivity measurements were carried out using solutions of varying concentrations of the swelling agents on a Toshniwal Conductivity Bridge type CLO1/0 1A. The cell constant was determined using the conductivity of N/50 KCl solution. The results were expressed in terms of specific conductivity on multiplying the reading by cell constant.

Determination of Acetyl Number. The acetyl number of swollen samples was determined by the method suggested by Warwicker.[7] The swollen sample, after washing with distilled water, was extracted with pyridine. Acetylation was then carried out in this medium using equal quantity of acetic anhydride. The amount of acetic acid combined was calculated by saponifying the acetylated sample followed by titration against standard HCl solution.

Measurement of Infrared Crystallinity Index. The infrared spectra of swollen cotton fibers were recorded on a Perkin-Elmer 21 double-beam spectrophotometer using the KBr disc technique.[8] The infrared crystallinity index was determined by taking the ratio of the peak intensities at 7.0–11.2 μ.

Determination of Moisture Regain. The moisture regain of the samples was determined at 75% RH and 30°C under conditions of adsorption. The accessibility of the swollen samples was calculated by using Valentine's equation.[9]

Extent of Swelling Measurements. The water of imbibition method was used to study the extent of swelling. Finely cut sample of about 0.5 g cotton fibers was thoroughly soaked in distilled water for about 2 h at 30°C. The sample was then transferred to a previously weighed centrifuging tube (W_1). The loosely

held water was driven out by centrifuging the sample at 3000 rpm for 30 min. The tube along with the sample was weighed accurately (W_2) followed by drying at 110°C for 18 h and weighed again (W_3).

The value of water of imbibition was calculated using the following equation:

$$\text{water of imbibition (\%)} = \frac{W_2 - W_3}{W_3 - W_1} \times 100$$

RESULTS AND DISCUSSION

In the present investigation, results with respect to swelling of cotton cellulose in aqueous solutions of benzylamine and 4-amino acetophenone dissolved in methanol have been discussed.

The —NH_2 group in the molecule of a swelling agent interacts with the cellulosic —OH groups during swelling of cotton cellulose with aliphatic monoamines. Morpholine was also shown to have strong interaction with the —OH groups of cellulose in the amorphous region.[6] Very little information, however, is available as regards the swelling mechanism of heterocyclic monoamines such as benzylamine and 4-amino acetophenone.

Swelling of Cotton with Benzylamine

Figures 1–4 give changes in moisture regain, water of imbibition value, acetyl number, and IR crystallinity index, respectively, against the change in the concentration of benzylamine in the swelling bath at 20°C and 35°C for 1 h. The moisture regain values remain almost unchanged up to the concentration of about 55% benzylamine beyond which they rise rapidly and attain a maximum at about

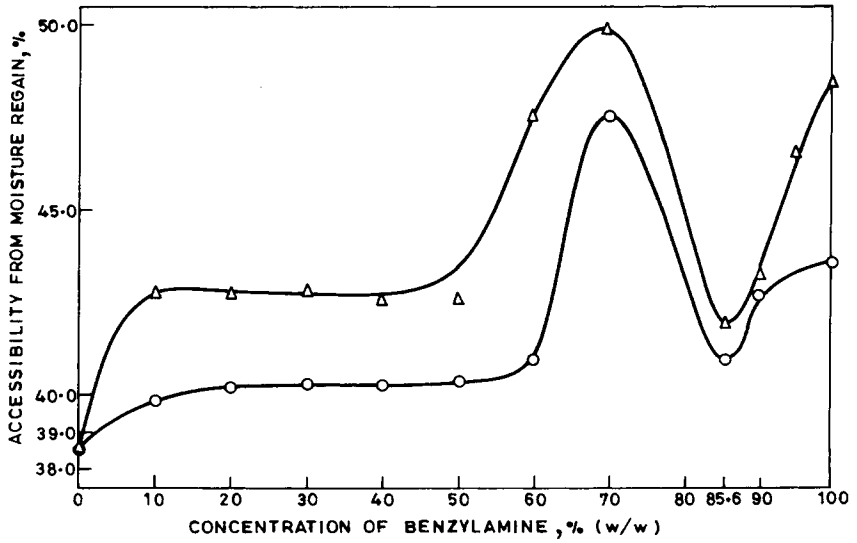

Fig. 1. Accessibility from moisture regain vs. concentration of benzylamine solutions: (○) 20°C; (△) 35°C.

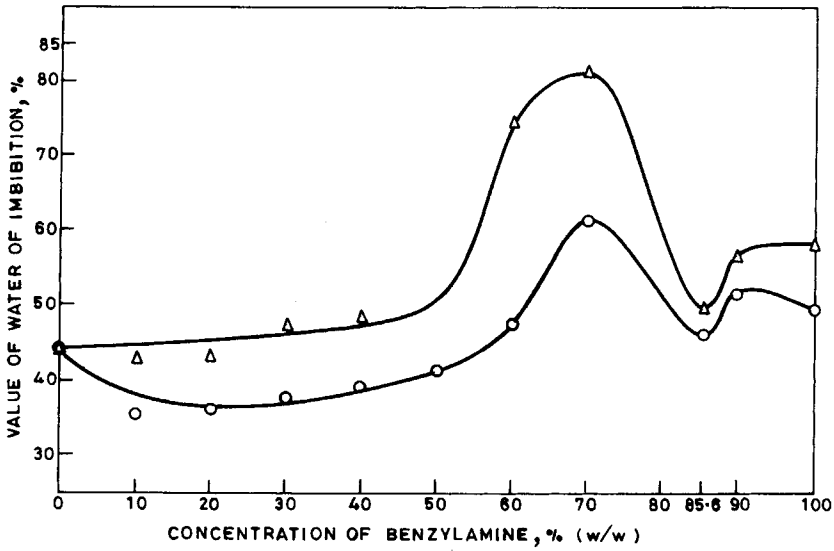

Fig. 2. Value of water of imbibition vs. concentration of benzylamine solutions: (○) 20°C; (△) 35°C.

70% concentration of the swelling agent. The values again drop with further increase in the benzylamine concentration and are minimum at 85.6%. This trend is common for both the temperatures of 20°C and 35°C, except that the absolute values for moisture regain at the latter temperature are higher than those at the former. This may be due to the higher kinetic energy of the benzylamine solutions at the higher temperature of 35°C. A very similar trend can be noticed with respect to the changes in the value of water of imbibition and acetyl number (Figs. 2 and 3). The IR crystallinity index is a measure of the crystalline portion present in the cotton sample. With the increase in the amount

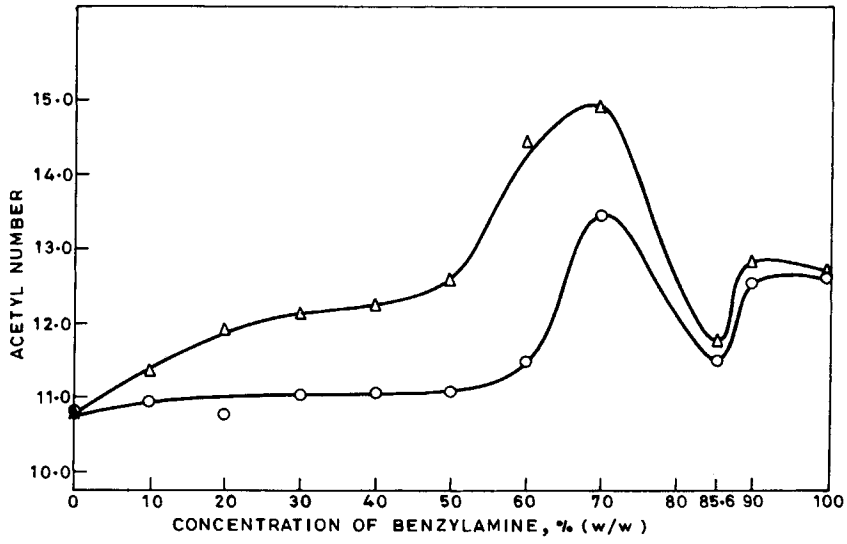

Fig. 3. Acetyl number vs. concentration of benzylamine solutions: (○) 20°C; (△) 35°C.

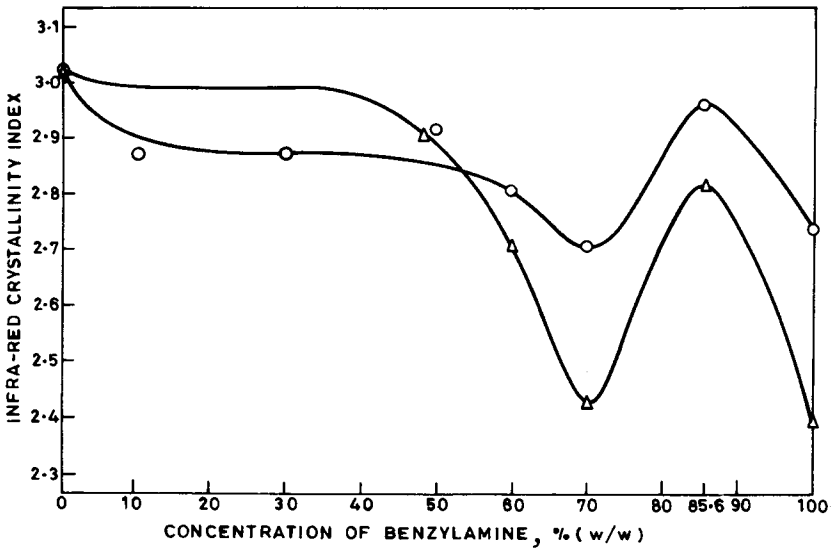

Fig. 4. IR crystallinity index vs. concentration of benzylamine solutions: (○) 20°C; (△) 35°C.

of swelling and decrystallization, the IR crystallinity index is reduced. The extent of this reduction shows the severity of the swelling treatment. From Figure 4, it can be seen that once again four distinct stages can be observed in the plot. The IR crystallinity index of 3.03 for the control drops to the minimum value of 2.71 at the critical concentration of 70% of the reagent, showing that a considerable amount of swelling and decrystallization has taken place at the critical concentration of 70% of benzylamine. The IR crystallinity index with respect to 85.6% benzylamine concentration is almost identical to that of the control, showing that it is the least effective concentration of the swelling agent.

The above trend in case of the IR crystallinity index at 35°C of treatment remains unaltered except that the IR crystallinity values drop further, showing more effectiveness of the swelling agent at the higher temperature of 35°C.

With a view to finding out the reason for the effectiveness or otherwise of aqueous solutions of benzylamine at different concentrations, conductivity studies were carried out taking different concentrations of benzylamine in water at 20°C and 35°C (Fig. 5). These results indicate specific breaks in the conductivity curve of benzylamine solutions. These breaks represent the specific interaction between the amine and the water molecules present in the solution. The break at 55% concentration gives the molar proportion of the reagent to water as 1:6, while at 60% and 85.6% the molar proportions are 1:4 and 1:1, respectively.

Benzylamine belongs to the family of alkylamines of the benzene series and resembles to an aliphatic amine. It is a strong base freely soluble in water. It is stronger than aniline and is only slightly weaker than ethylamine. As the amino group is attached to a carbon atom adjacent to the ring, it behaves like a primary amine. It can be looked upon as a substituted methylamine in which a hydrogen atom in the alkyl chain is substituted by a phenyl group. This re-

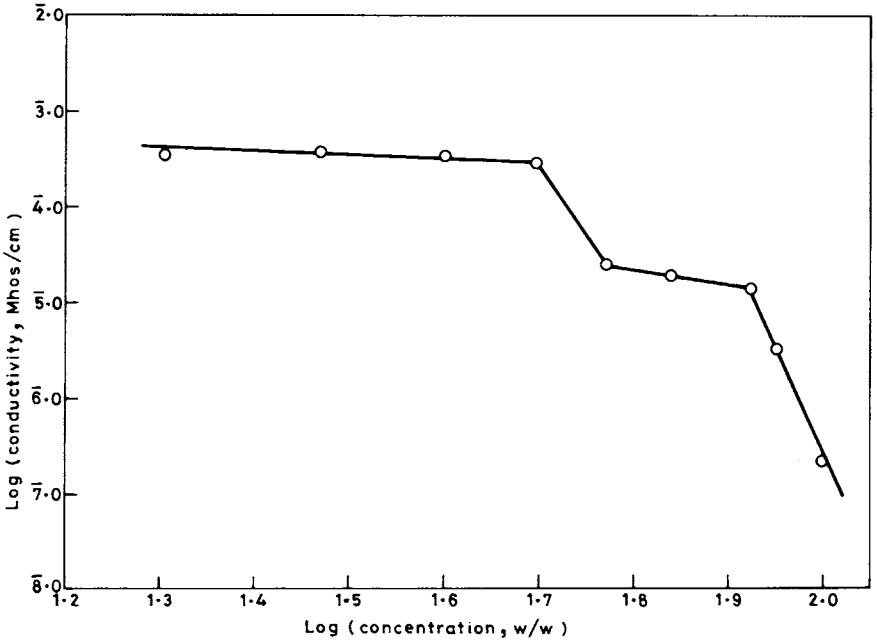

Fig. 5. Log (specific conductivity) vs. log (concentration of benzylamine solution): (○) 20°C; (△) 35°C.

placement, however, causes a change in the basicity of the amine, and, hence, benzylamine gives a lower K value (K values of methylamine, ethylamine, and benzylamine are 50×10^{-5}, 56×10^{-5}, and 2.29×10^{-5}, respectively). This is attributed to the withdrawal of the electron density from the nitrogen atom through the inductive effect of the phenyl group. Hyperconjugation of the methylene group to the aromatic ring also plays an important role. Possibly the electron-donating character of the methylene group could be one of the important factors in imparting a fairly strong basic character to benzylamine.

In this respect, the comparison of the swelling action of ethylamine and benzylamine on cotton will be interesting. A considerable amount of work has been done on ethylamine as a swelling agent for cotton cellulose, and the swelling mechanism has been described in terms of the strong interaction between the primary amine and water molecules forming hydrates in the solution. At 71.4% concentration, ethylamine was shown to form monohydrates in water and was found to be ineffective in having interaction with the —OH groups of cellulose. With the result, this critical concentration of the reagent could not bring about any appreciable amount of swelling and decrystallization of cotton cellulose. Beyond the monohydrate stage, the amino groups in the ethylamine molecules became free, and correspondingly higher amounts of the amine–cellulose complex were formed giving appreciable amount of swelling and decrystallization.[1]

Benzylamine solutions up to a concentration of 55% do not bring about any appreciable swelling of cotton cellulose, showing that all the possible sites in the benzylamine molecule might have been blocked. Interestingly, the corresponding molar ratio of benzylamine with water is exactly 1:6. Thus, it is likely that six water molecules are associated with the six possible sites (five CH groups

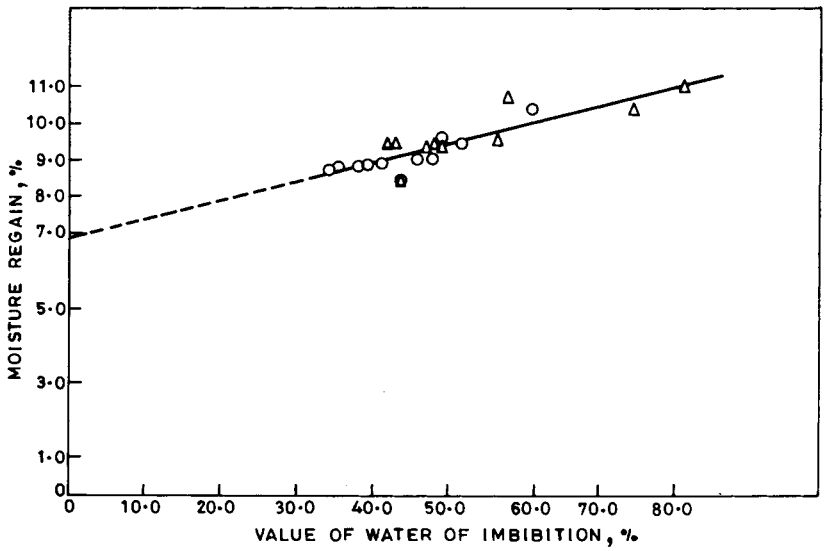

Fig. 6. Correlation between moisture regain values and value of water of imbibition: (○) 20°C; (△) 35°C.

of benzene ring and one —NH_2 group in the side chain) in the benzylamine molecule. Thus, the hydrated amino group is unable to bring about the swelling of cotton cellulose. Beyond this stage, the number of water molecules are insufficient to block all the possible six sites in the benzylamine molecule, leaving at least a few amino groups free. With the increase in the concentration of the reagent, the possibility of the number of free amino groups present in the benzylamine solution increases, giving more and more active species which form the amine–cellulose complex, resulting in the swelling and decrystallization of cotton fibers. The results in the present investigation indicate that the maximum extent of swelling occurs in the region of 60–70% concentrations of benzylamine. At 60% and 70% concentrations, the molar ratios of benzylamine with water are 1:4 and 2:5, indicating that maximum number of free amino groups are present in this concentration range of benzylamine, and, therefore, the swelling of cotton is also of the highest order. The ineffectiveness of 85.6% concentration of benzylamine may be attributed to the amine:water ratio of exactly 1:1. At this concentration, it seems that, due to greater affinity of amino nitrogen for water molecules, almost all the water molecules are associated with the amino groups of benzylamine and, hence, such a solution may be ineffective in the formation of the amine–cellulose complex as well as in having the swelling and decrystallizing effect on cotton fibers.

Correlation Characteristics

Figure 6 shows a correlation between the moisture regain values and those of water of imbibition for the benzylamine-swollen cotton fibers. It is a linear plot giving good correlation between these two characteristics. On extrapolation, the plot gives an intercept at 7.0% moisture regain value. Thus, for the zero value of water of imbibition the swollen fibers give 7.0% moisture regain, which cor-

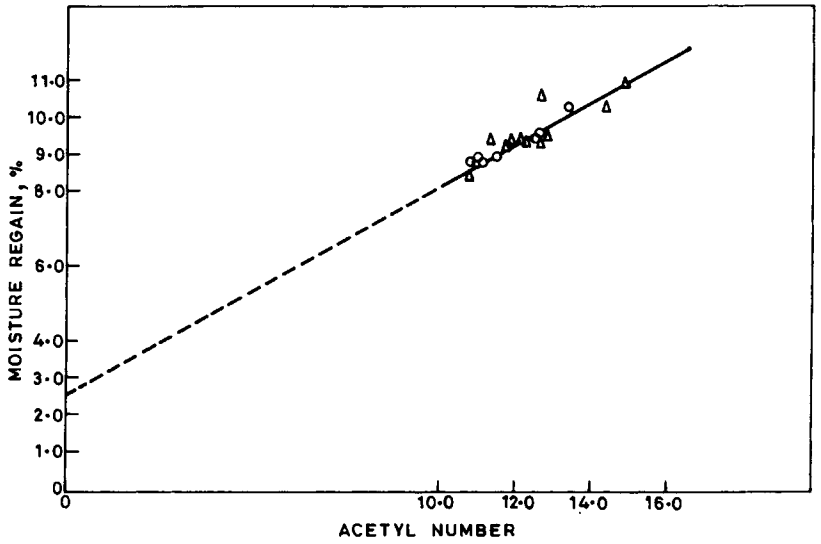

Fig. 7. Correlation between moisture regain values and acetyl number: (○) 20°C; (△) 35°C.

responds to the normal moisture content of cotton fibers. The swelling and decrystallizing action of benzylamine solutions on cotton produces a fiber structure, in which the voids inaccessible to liquid water are made accessible to the water vapor.

A good linear correlationship exists between the absorption characteristic (moisture regain) and chemical reactivity (acetyl number) of the benzylamine-treated cotton fibers (Fig. 7). On extrapolation, the plot gives an intercept at about 2.5% moisture regain, showing that there is still some amount of moisture

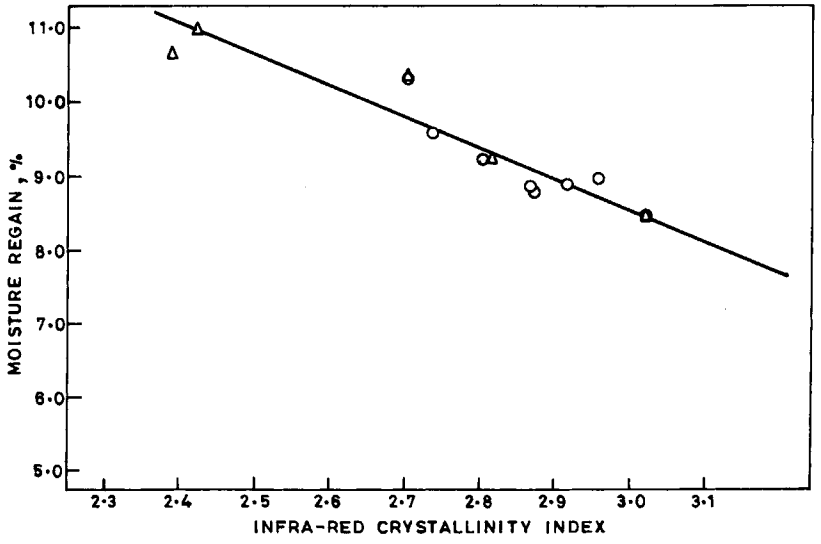

Fig. 8. Correlation between moisture regain values and IR crystallinity index: (○) 20°C; (△) 35°C.

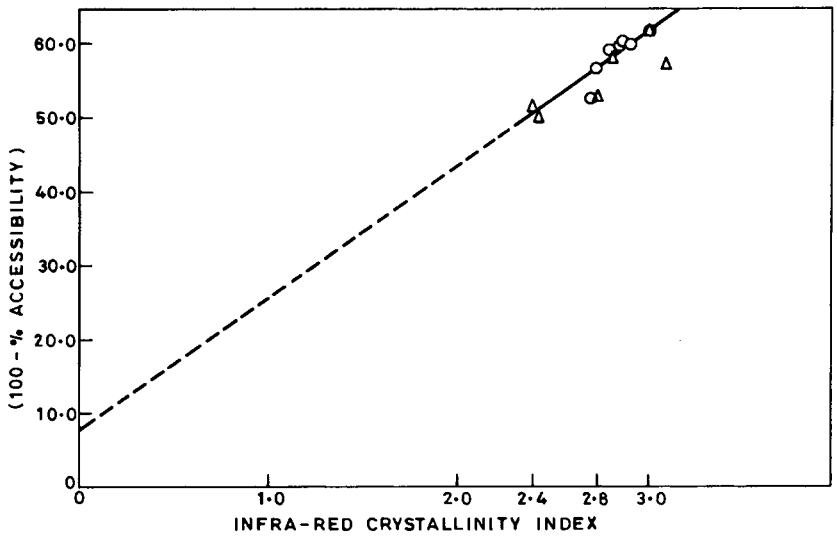

Fig. 9. Correlation between crystallinity and IR crystallinity index: (○) 20°C; (△) 35°C.

present in the sample for zero acetyl number. Both the properties are closely connected with the accessible hydroxyl groups in cellulose. Acetyl number, however, gives a better quantitative representation of chemical reactivity of the —OH groups in cellulose. The moisture regain of cellulose largely shows the extent of absorption of water vapor in the amorphous regions; there are, however, still some other sites in cellulose structure which accommodate additional moisture in the fiber, e.g., fine capillaries and mesomorphous regions. Such

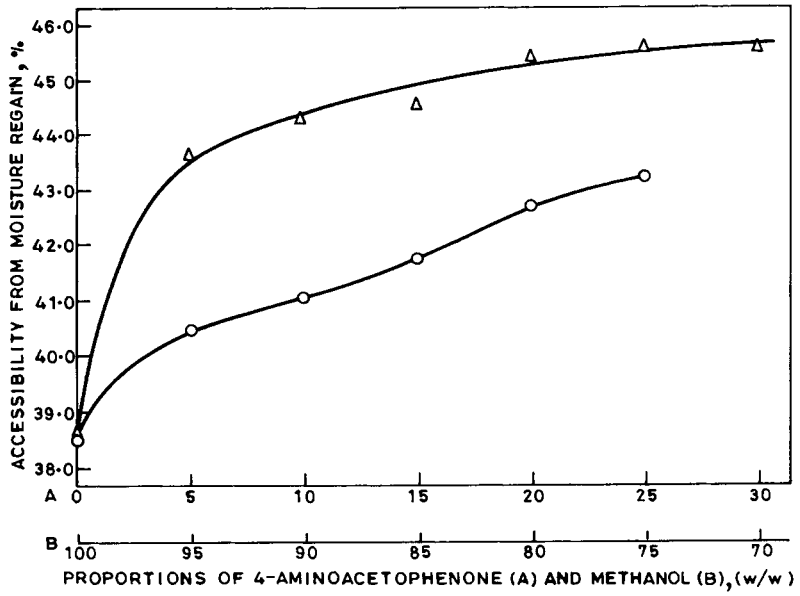

Fig. 10. Accessibility from moisture regain vs. concentration of 4-amino acetophenone solutions: (○) 20°C; (△) 35°C.

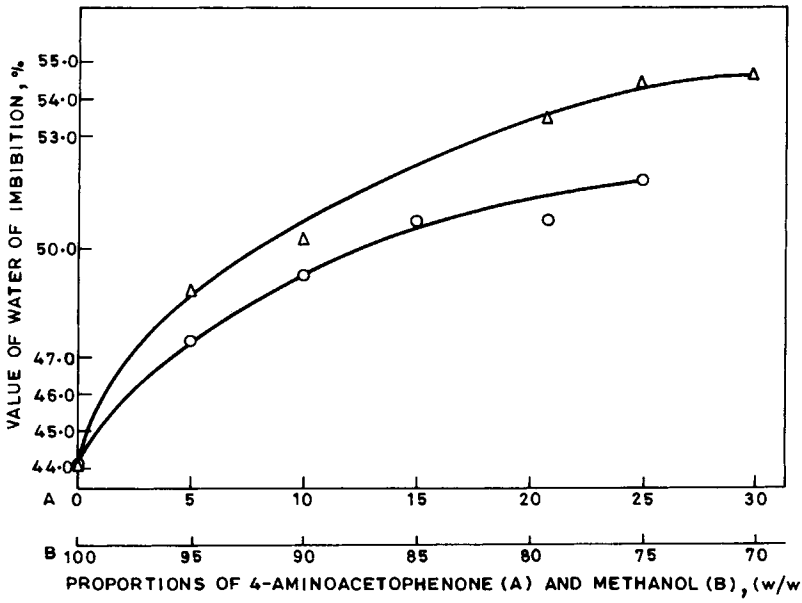

Fig. 11. Value of water of imbibition vs. concentration of 4-amino acetophenone solutions: (O) 20°C; (Δ) 35°C.

regions, although accessible to water vapor, are resistant to acetylation reaction due to the inaccessibility of the hydroxyl groups present in these regions to comparatively larger acetylating reagent molecules.

Changes in the crystalline portion of cotton fibers can be studied by determining the IR crystallinity indices of swollen samples. The correlation between

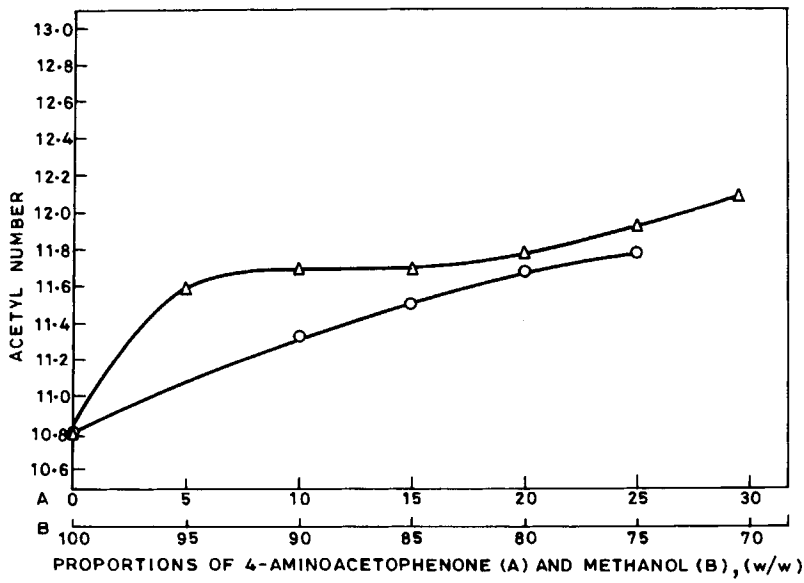

Fig. 12. Acetyl number vs. concentration of 4-amino acetophenone solutions: (O) 20°C; (Δ) 35°C.

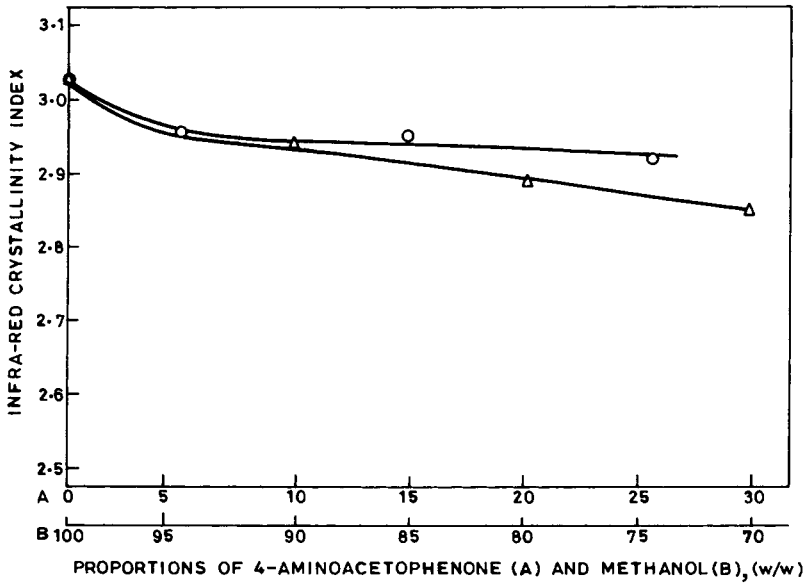

Fig. 13. IR crystallinity index vs. concentration of 4-amino acetophenone solutions: (○) 20°C; (△) 35°C.

the moisture regain and the IR crystallinity index has been shown in Figure 8. The linear plot shows that both the properties can be correlated, since decrease in the crystalline portion will proportionately lower the IR crystallinity index and increase the amorphous portion, giving proportionately higher moisture regain. This can be further confirmed from Figure 9, showing a good linear correlation plot between the residual crystallinity in the benzylamine-treated cotton samples and their IR crystallinity indices.

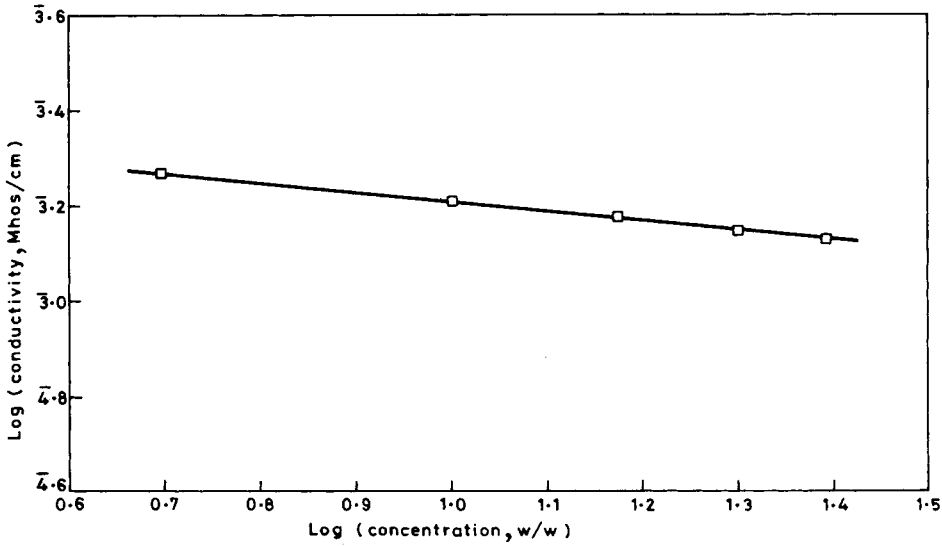

Fig. 14. Log (specific conductivity) vs. log (concentration of 4-amino acetophenone solutions): (○) 20°C; (△) 35°C.

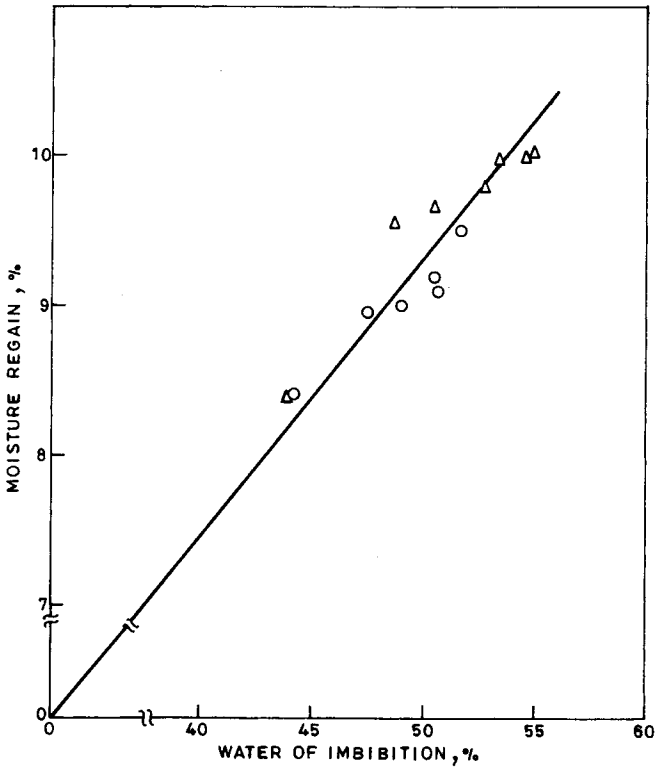

Fig. 15. Correlation between moisture regain values and value of water of imbibition: (○) 20°C; (△) 35°C.

Swelling of Cotton with 4-Amino Acetophenone

4-Amino acetophenone is sparingly soluble in water, and, therefore, its swelling action on cotton fibers has been studied using its methanol solutions of different concentrations at 20°C and 35°C for 1 h. Figures 10–13 show different characteristics of 4-amino acetophenone-treated cotton fibers at different concentrations in methanol at 20°C and 35°C. The accessibility from moisture regain increases marginally with increase in the concentration of the swelling agent (Fig. 10). A similar trend can be seen in the case of water of imbibition and acetyl number characteristics (Figs. 11 and 12). The IR crystallinity index remains almost steady at different concentrations of the swelling agent, indicating that it fails to penetrate in the ordered regions of cellulose without effecting any decrystallization of the fibers. It seems, therefore, that 4-amino acetophenone mainly operates in the existing amorphous regions of cellulose, which is reflected in the increase in the moisture regain values, water of imbibition, and acetyl number to a certain extent.

4-Amino acetophenone, with its limited solubility in methanol at the temperatures of the treatment followed in this investigation, could give solutions up to only 30% (w/w) at 35°C. The molar proportion of 4-amino acetophenone to methanol at this concentration is of the order of 1:10, and, hence, probably it is too low to bring about appreciable swelling and decrystallization of cellulose.

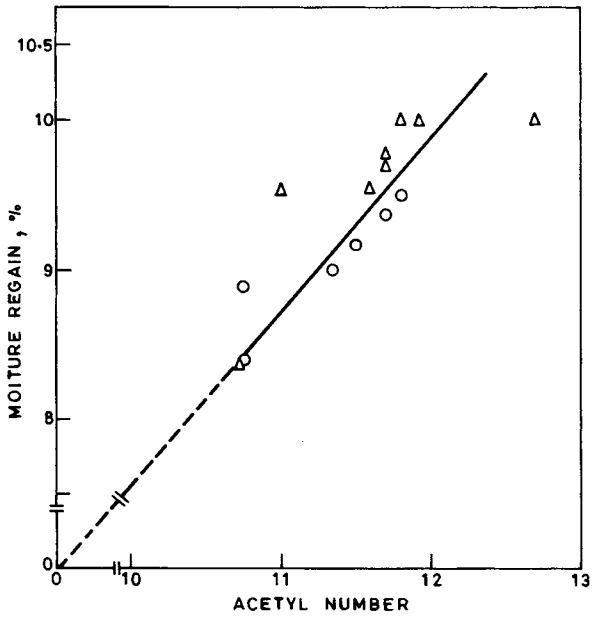

Fig. 16. Correlation between moisture regain values and acetyl number: (○) 20°C; (△) 35°C.

The conductivity measurements of 4-amino acetophenone in methanol at 20°C and 35°C reveal that there is no break in the conductivity curve and, hence, there may not be present a specific strong interaction between 4-amino acetophenone and methanol molecules at any particular concentration of the reagent (Fig. 14). The solutions at 35°C are somewhat more effective than those at 20°C due to the higher thermal energy of the swelling bath.

Figures 15 and 16 give the correlation between moisture regain and water of imbibition, and moisture regain and acetyl number, respectively. It can be said that these properties are very well correlated, giving linear plots. The interesting feature of these correlation plots is that, on extrapolation, they pass through the origin. These results indicate that, for zero value of water of imbibition as well as for zero acetyl number, the moisture regain is also zero. Since 4-amino acetophenone molecules bring about the swelling action only in the amorphous regions and without accompanying decrystallization of cotton fibers, some of those regions which, although accessible to water vapor but inaccessible to liquid water as well as to the acetylating agents in the control samples, are opened up further by the swelling action of 4-amino acetophenone, so that all the accessible hydroxyl groups in the swollen sample are equally accessible to water vapor, liquid water as well as to the acetylating reagents.

4-Amino acetophenone can be looked upon as modified aniline, in which the acetyl and the amino groups are in the *para* position. The K value for aniline is of the order of 4×10^{-10}, which shows that aniline is much weaker base than alkylamines and even benzylamine itself. The basic character of aniline is further reduced by the substituent group —$COCH_3$ in the benzene ring at the *para* position to the amino group. The acetyl group in this position is itself deactivating and *meta*-directing, giving mesomeric polarization of the arylamine.[10]

With the result, the *para* position loses its activity to a considerable extent, making the amino group in 4-amino acetophenone much weaker in its basic character as compared to the one present either in aniline itself or in the benzylamine molecule. This explains the intra- and intercrystalline swelling action of benzylamine and 4-amino acetophenone, respectively.

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