Swelling Behavior of Cotton Fibers in Morpholine and Piperidine

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Synopsis

Solution properties (conductivity and refractometry) of aqueous solutions of morpholine and piperidine as well as their aqueous mixtures with model compounds (glucose, cellobiose, xylose, and cellobiose octaacetate) in varying molar ratios were studied. The possible mechanism of the unique swelling action of morpholine on cotton cellulose and the total inaction of piperidine was investigated. It was shown that the solubility parameter (δ) may not fully indicate the swelling ability of a reagent, but the H-bonding portion (δH) and polar part (δp) of δ are of importance. Morpholine possesses a higher value of δH + δp than does piperidine; hence it is a powerful swelling agent for cellulose. It produces over 200% swelling at the interfibrillar level and has the ability to decrystallize cellulose under certain favorable conditions.

INTRODUCTION

A number of organic compounds such as diamines, aliphatic monoamines and quaternary ammonium compounds, and sodium hydroxide, zinc chloride, liquid ammonia, and mineral acids have been investigated in the past as swelling agents for cellulose. Very little work, however, has been reported on the swelling action of cyclic monoamines on cotton cellulose. We have reported the unique swelling action of morpholine on cotton cellulose at the microfibrillar level as well as its synergistic influence in producing enhanced swelling and decrystallization of cotton cellulose in conjunction with other swelling agents.[1,2] It was also observed that not only the direct dye uptake of the morpholine-treated cotton fiber but also its dyeability with reactive dyes increased.[3] This was attributed to the conversion of pseudocrystallites present in the disordered regions as well as on the crystallite surfaces.

Work from other laboratories has also confirmed the powerful swelling action of morpholine on cotton cellulose.[4] Philipp, Schleicher, and Wagenknecht[5] in their study on swelling of cellulose in various liquids including morpholine observed that the extent of swelling was dependent on the cellulose structure as well as the molar volume and the solubility parameter δ of the liquid, especially its hydrogen bonding part δH and the polar part δp. No data, however, have been reported so far on the swelling ability of piperidine on cotton cellulose.

The aim of the present investigation was to study the swelling effects of morpholine and piperidine on cotton. Results with other cyclic monoamines will be reported subsequently.

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EXPERIMENTAL

Materials

Cotton Cellulose. Good-quality, long-stable Sudanese cotton in loose form was purified according to the standard procedure. The scoured and bleached cotton cellulose had a D.P. of 2250, a copper number of 0.01, and a carboxyl content of 0.3 meq/100 g cotton.

Chemicals. The KBr used for the preparation of pellets for infrared spectroscopy and the D-glucose, xylose, cellobiose, and cellobiose octaacetate (COA) used in the conductivity and refractive index measurement studies were of Analar grade. All other chemicals including morpholine and piperidine were of C.P. grade. The reagents were distilled before use.

Methods

Conductivity Measurements. The conductivity measurements were carried out using high-purity conductivity water on a Philips PR 9500-type conductivity bridge at 25°C using varying concentrations of the swelling agent as well as model compound. The cell constant was determined using the conductivity of a $N/50$ KCl solution. Results were expressed in terms of specific conductivity.

Determination of Refractive Index. Refractivity measurements of mixtures of model compounds for cellulose in solutions of swelling agents of varying concentrations were carried out at a constant temperature of 25°C using the Abbé refractometer manufactured by Erma, Tokyo (Japan). Refractive indexes (n) were directly read on the scale of the refractometer.

Preparation of Swollen Cotton Fibers. Purified cotton cellulose was treated with aqueous solutions of morpholine and piperidine of varying concentrations covering the whole range from 0 to 100% at 20°C for 1 hr. At the end of the treatment, the samples were washed repeatedly with distilled water. Excess water was removed by squeezing and the last traces of water removed progressively by displacement, first by dry methanol and then by dry ether followed by air drying. A few samples were similarly prepared by treating cotton fibers in 40% (w/w) morpholine solution at 20° and 35°C for 1 hr.

Surface Area Measurement. The internal surface of a few samples treated with morpholine was measured by the standard nitrogen absorption method.

Determination of Extent of Swelling. The propanol-2 retention method suggested by Andrews and Oberg[6] was employed and the extent of swelling expressed in terms of the milliliters of propanol-2 absorbed by 100 g fiber at 30°C.

Measurement of Microfibrillar Dimensions. Electron micrographs of morpholine (40%)- and piperidine (60%)-treated cotton fibers, were obtained by the method described by Preston,[7] and width and thickness of the microfibrils were measured.

Determination of Density of Cotton Fibers. The density of cotton was determined using the density gradient tube, and crystallinity was calculated by the method suggested by Preston and Nimkar.[8]

Infrared Crystallinity Index Measurement. Infrared spectra of cotton fibers were recorded on a Perkin-Elmer 21 double-beam spectrophotometer using the KBr disc technique.[9] The infrared crystallinity index was determined by the ratio of peak intensities at 7 to 11.2 μ.

RESULTS AND DISCUSSION

The $-NH_2$ in the molecule of the swelling agent interacts with the cellulosic —OH group during the swelling of cotton cellulose with aliphatic monoamines. There is, however, little information available as regards the swelling mechanism of cyclic monoamines such as morpholine and piperidine.

Table I shows the manner in which morpholine induces the swelling of cotton fibers. From the results of density and infrared crystallinity index measurements, it can be seen that morpholine fails to penetrate the ordered regions of cellulose. The samples treated at 35°C for 25 hr also showed similar results. The morpholine-treated sample, however, has increased internal surface area and enlarged microfibrillar dimensions and shows greater propanol-2 retention. This suggests that morpholine brings about changes in the disordered regions of cellulose, and the extent of intercrystalline swelling is of the order of 200%. The unique nature of morpholine action on cotton cellulose lies in the fact that the swelling produced is similar to that produced during the mercerization process, but without any decrystallization.

Table II shows the results of piperidine treatment on cotton cellulose. It can be seen that this reagent neither brings about decrystallization nor any swelling at the interfibrillar level in cotton fibers. Thus piperidine differs basically from morpholine in regard to its swelling influence on cellulose, although the two cyclic monoamines are identical in their chemical structure except that the oxygen in the para position to the amino group in the morpholine molecule has been replaced by a $>CH_2$ group. Figure 1, which shows the electron micrographs of the control as well as the morpholine- and piperidine-treated cotton fibers, also indicates that the morpholine-treated sample has a completely open structure with enlarged microfibrils, in contrast to the piperidine-treated sample in which the microfibrils have almost the same dimensions as that in the control.

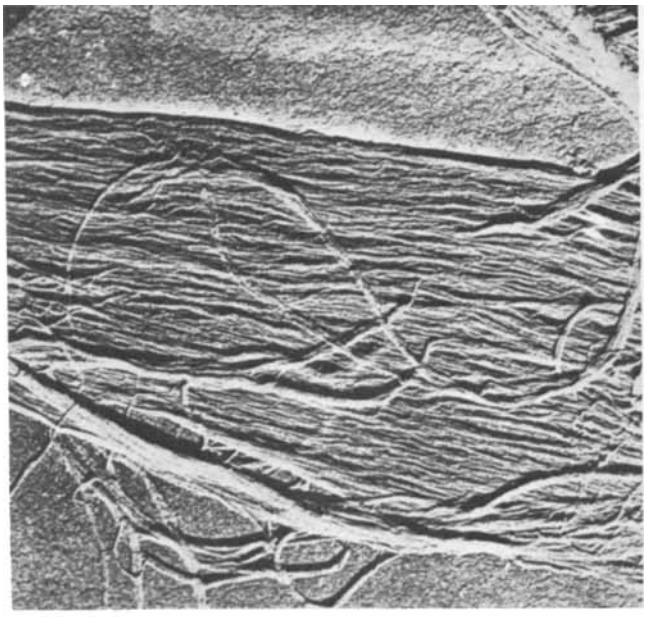
Conductivity measurements and refractometric analysis were carried out on aqueous solutions of the monoamines in the presence of model compounds for

TABLE I
Extent of Swelling of Cotton in 40% Aqueous Morpholine Solution at 20°C for 1 hr

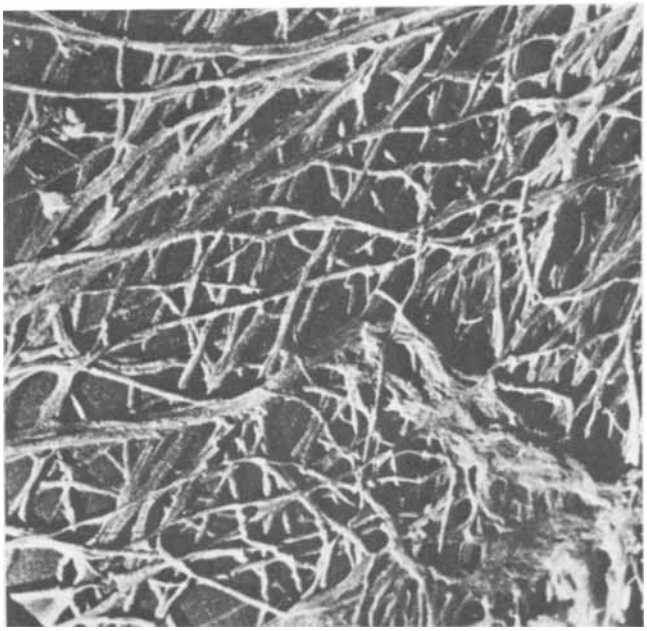
	Surface area, m^2/g	Propanol-2 retention, ml/100 g	Microfibrillar dimensions, Å		Density, g/cm^3	Crystallinity from density, %	Infrared crystallinity index
			Width	Thickness			
Control sample	4.0	17.2	11.0	25.0	1.5502	69.0	3.00
Swollen sample	9.0	33.5	20.5	50.0	1.5500	68.5	2.95
Extent of swelling, %	225	195	186	200	—	—	—
Decrystallization, %	—	—	—	—	nil	nil	nil

TABLE II
Extent of Swelling of Cotton in 60% Aqueous Piperidine Solution at 20°C for 1 hr

	Propanol-2 retention, ml/100 g	Microfibrillar dimensions, Å		Density, g/cm^3	Crystallinity from density, %	Infrared crystallinity index
		Width	Thickness			
Control sample	17.2	11.0	25.0	1.5502	69.0	3.00
Swollen sample	17.2	11.5	25.0	1.5502	69.0	3.00
Extent of swelling, %	negligible	nil	nil	—	—	—
Decrystallization, %	—	—	—	nil	nil	nil

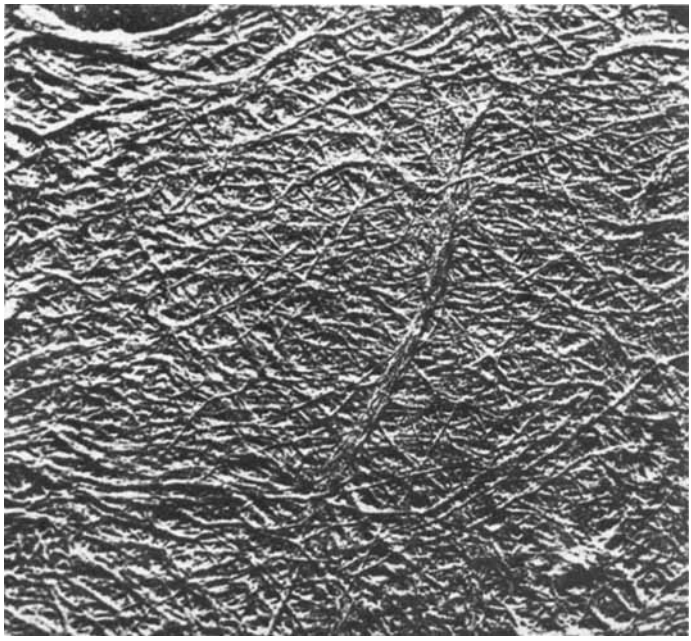


(a)



(b)

Fig. 1. Electron micrographs of cotton fibers (Au–Pd shadowed): (a) control (×38,230); (b) morpholine treatment (40%, 1 hr, 20°C) (×37,000); (c) piperidine treatment (80%, 1 hr, 20°C) (×27,780).



(c)

Fig. 1. (Continued from the previous page.)

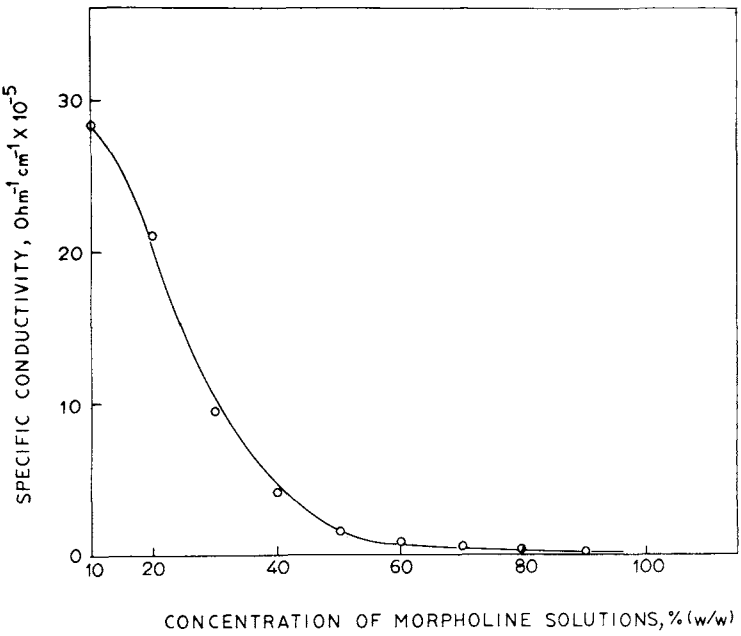


Fig. 2. Specific conductivity vs concentration of morpholine solutions.

cellulose, viz., glucose, cellobiose, xylose, and cellobiose octaacetate (COA). Glucose is a basic constituent of the cellulose chain molecule, while cellobiose is believed to be a true repeat unit. Both compounds contain three OH groups (one primary and two secondary) of the anhydroglucose unit of cellulose. Although xylose is isomorphous to glucose and to the anhydroglucose residue in

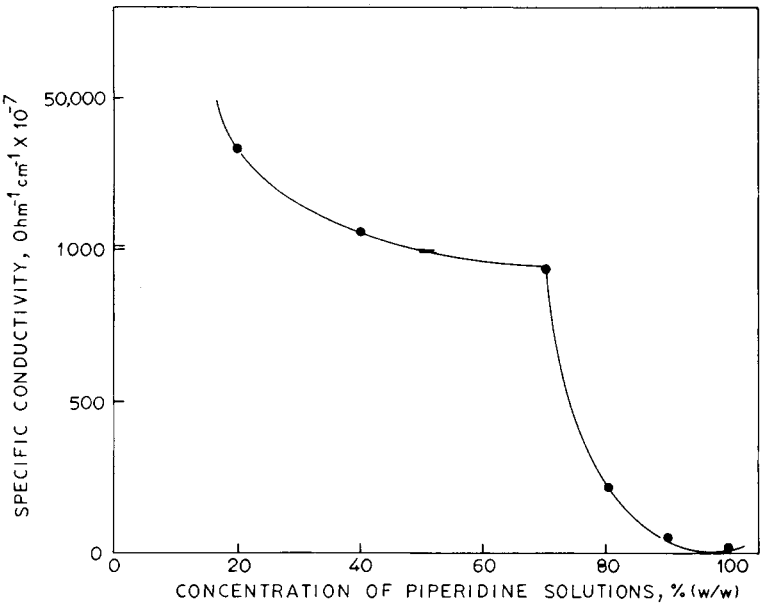


Fig. 3. Specific conductivity vs concentration of piperidine solutions.

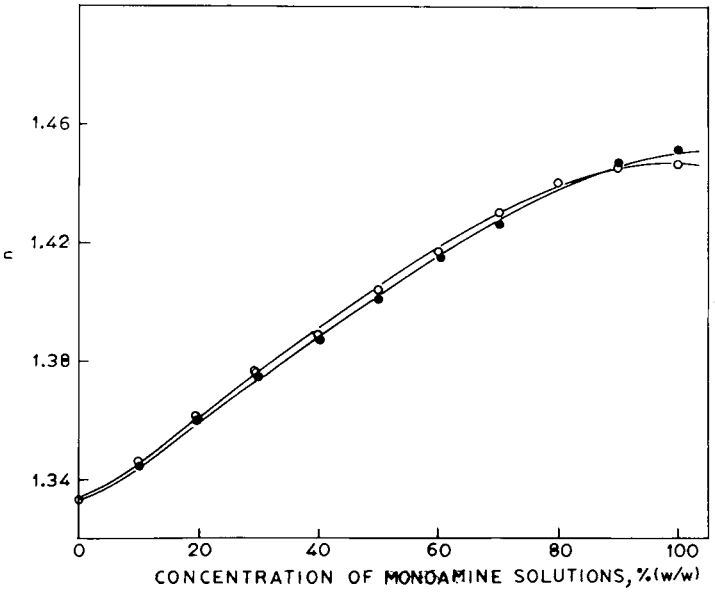


Fig. 4. Refractive index vs concentration of morpholine (○) and piperidine (●).

cellulose, it contains only secondary OH groups at C_2 and C_3, but is devoid of the primary OH at C_6. In COA, all the OH groups are acetylated, thus leaving no OH groups capable of interaction with polar liquids.

Figure 2 shows a plot of specific conductivity versus morpholine concentration. A smooth curve without any sharp break suggests that morpholine does not form specific hydrates in the aqueous solutions. The same can be said about piperidine (Fig. 3). Figure 4 gives results of refractive index measurements for the two reagents. The conductivity and refractive index measurement studies show

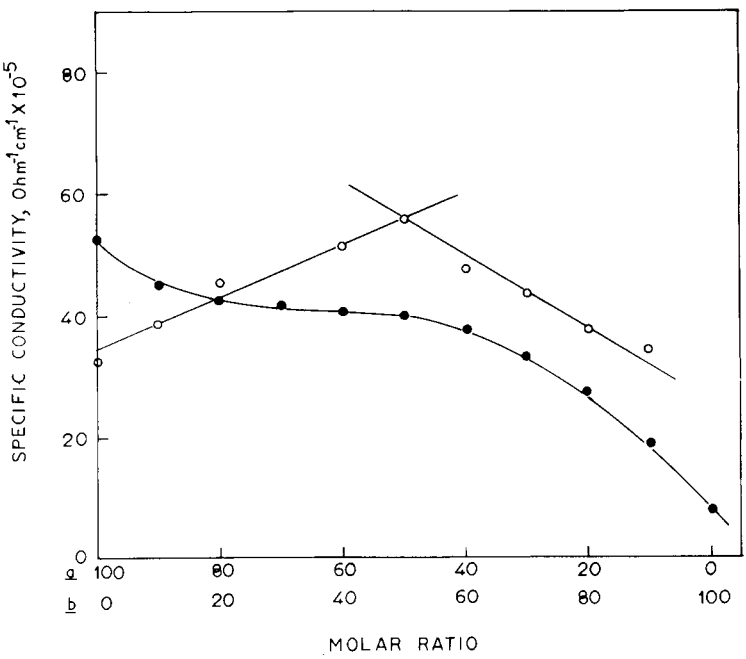


Fig. 5. Specific conductivity vs molar ratio (a/b): (O) morpholine (total molarity 0.1M); (●) piperidine (total molarity 1.0M); (a) cyclic amine; (b) glucose.

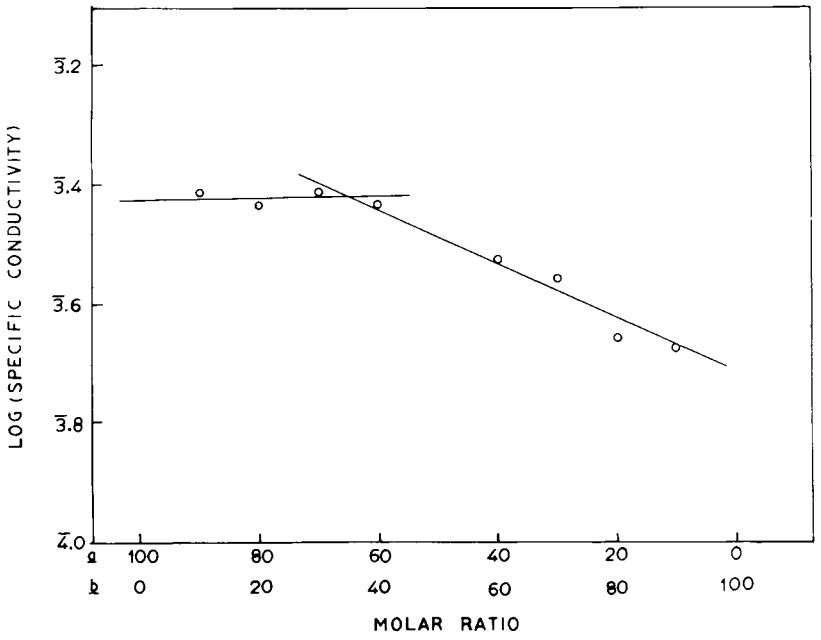


Fig. 6. Plot of log (specific conductivity) vs molar ratio (a/b) (total molarity 0.1M): (a) morpholine; (b) cellobiose.

that both morpholine and piperidine are alike in that neither has strong interaction with water molecules comparable to the one existing between EDA and water.

Figure 5 shows the plots of specific conductivity versus molar ratio of a monoamine and glucose. While a sharp break in the plot is observed at a 1:1 molar ratio in the case of morpholine–glucose mixtures, no such break is observed in the case of the piperidine–glucose system. These results clearly show that a morpholine molecule has a strong interaction with a glucose molecule and the two reagents form a 1:1 complex. This suggests that the >NH group of morpholine has a strong interaction with only one OH group of the glucose molecule. Piperidine, on the other hand, does not possess such an ability to undergo a complex formation with glucose. Similar observations were made when conductivity measurements were carried out using the morpholine–cellobiose system with varying molar ratios (Fig. 6). The results indicate an interaction between two molecules of morpholine per cellobiose molecule, suggesting a 1:1 complex between morpholine and glucose residue. Under unfavorable conditions, however, one of the two possible interaction sites in the cellobiose molecule might be left vacant, in which case a weak tendency of 1:1 interaction can also be seen.

Figures 7 and 8 give the results of the refractometry of morpholine–glucose and morpholine–cellobiose systems. In these cases also, a 1:1 complex between morpholine and glucose as well as a 2:1 complex between morpholine and cellobiose can be seen. The path of the light is deviated at the molar ratio at which the complex is formed to the maximum extent between morpholine molecules and the two polysaccharides.

It is likely that the primary OH at C_6 in glucose as well as in cellobiose molecules is the most reactive among the OH groups present in the two reagents, and hence the morpholine molecules form a complex with the primary OH of the polysaccharides through its >NH group. Creely et al.[10] have similarly reported that a complex was formed between ethylenediamine and cellulose. A 2:1 ratio

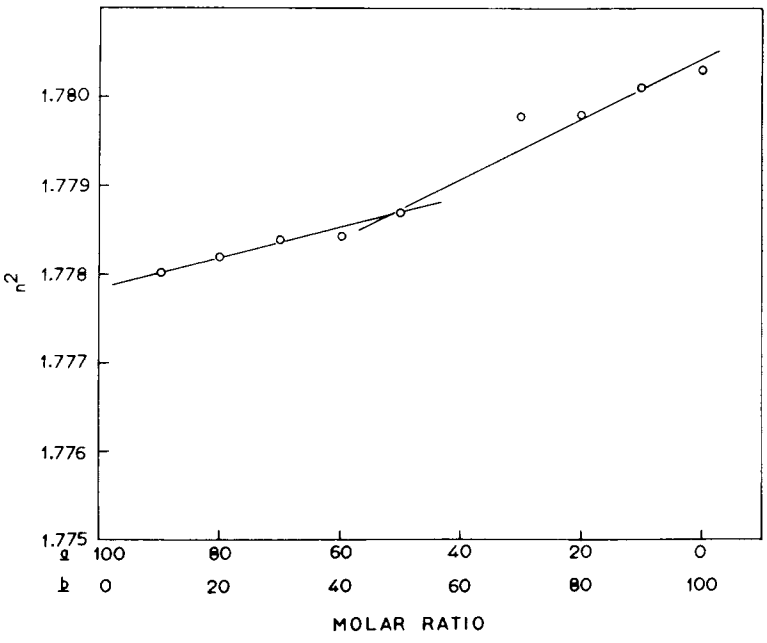


Fig. 7. Plot of n^2 vs molar ratio (a/b) (total molarity 0.1M): (a) morpholine; (b) glucose.

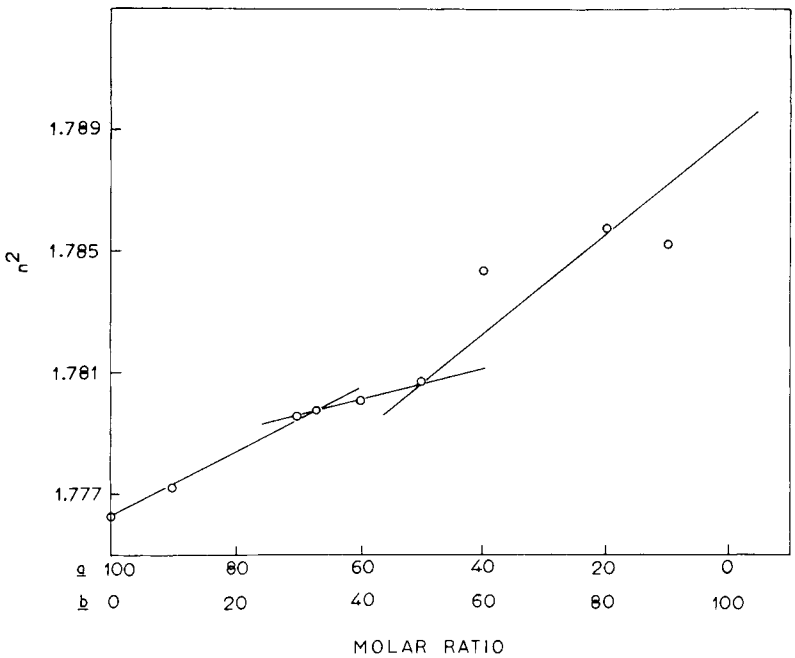


Fig. 8. Plot of n^2 vs molar ratio (a/b) (total molarity 0.1M): (a) morpholine; (b) cellobiose.

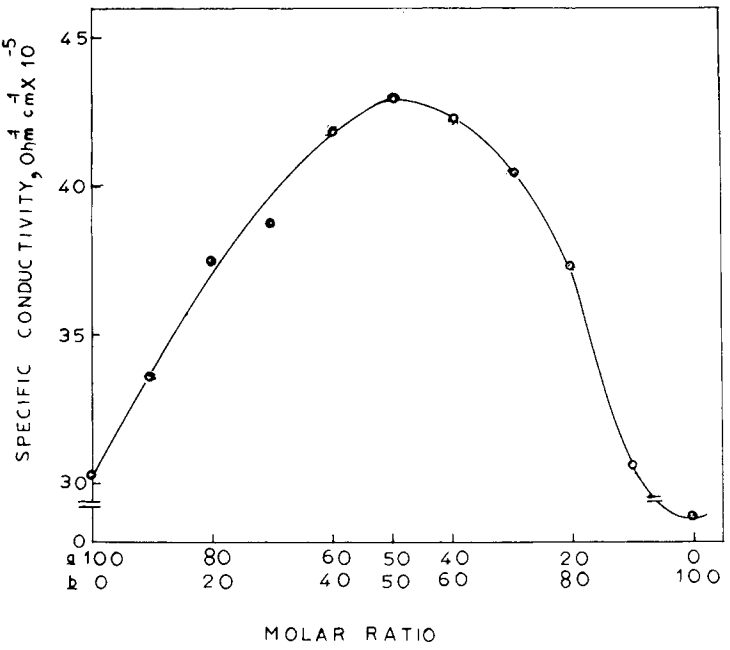


Fig. 9. Specific conductivity vs molar ratio (a/b) (total molarity 0.1M): (a) morpholine; (b) xylose.

existed between the anhydroglucose units and the diamine molecules, indicating that one diamine molecule was crosslinking two cellulose chains through H bonding, chiefly through the primary hydroxyls.

In order to verify the above observation, conductometric measurements were

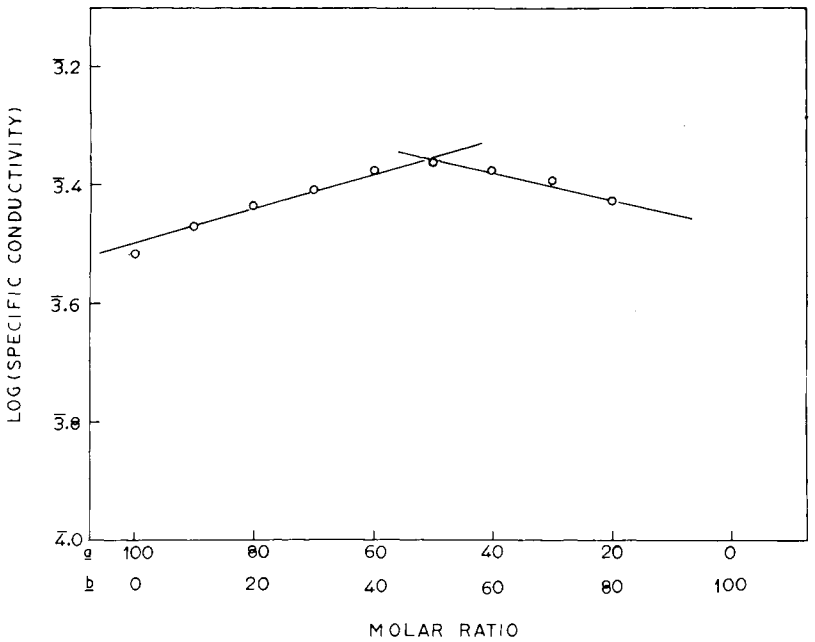


Fig. 10. Plot of log (specific conductivity) vs molar ratio (a/b) (total molarity 0.1M): (a) morpholine; (b) xylose.

carried out using the morpholine–xylose system of varying molar proportions. When the specific conductivity was plotted against the molar ratio, the break was again at the 1:1 molar ratio; however, the break was not as sharp as in the morpholine–glucose system, suggesting that in the absence of the primary OH group in the polysaccharide molecule the interaction is much weaker (Figs. 9 and 10). It seems that out of the two secondary OH groups present in xylose, the one presumably at C_2, which interacts more frequently, forms a labile complex with the morpholine molecule.[11,12]

In order to ascertain the above contentions, the morpholine–COA system was investigated (Fig. 11). Although there is no strong interaction between morpholine and COA, there is, however, a faint tendency of association between the two at a ratio of 2:1. The absence of any strong interaction between the morpholine and COA confirms that the OH is the site of complex formation between the morpholine molecule and the carbohydrate. A very weak interaction between morpholine and COA in the 2:1 proportion suggests that the ring oxygen in the glucose residue might be the possible site.

The results of the present investigation indicate that both morpholine and piperidine are alike in that neither one forms hydrates with water. The two reagents, however, differ from each other in their H bonding capacity with OH groups in a polysaccharide or in cellulose, since morpholine possesses a stronger H bonding capacity than piperidine. This can be supported by comparing the hydrogen bonding part (δH) of the solubility parameters of the two reagents: δH for morpholine (4.92) is much higher than that for piperidine (2.82).[13]

It should be emphasized that interaction between monoamines and a strongly H-bonded substance such as cotton assumes a higher complexity. No simple correlation is obtained between the swelling of such polymers and data commonly

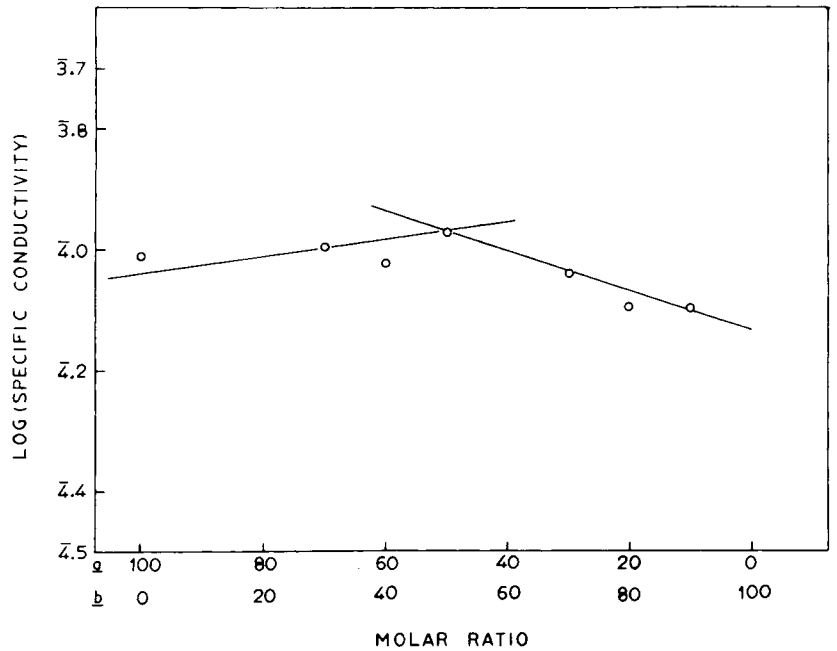


Fig. 11. Plot of log (specific conductivity) vs molar ratio (a/b) (total molarity 0.01M): (a) morpholine; (b) COA.

used to characterize intermolecular interactions such as the dielectric constant, dipole moment, and even solubility parameter (δ). In order to characterize the extent of swelling of cotton cellulose in monoamines, contributions of three important factors must be considered: (1) the supermolecular structure of fibers, (2) the molar volume of the solvent (V_m), and (3) the hydrogen bonding part (δH) and polar part (δp) of the δ of the solvent. With comparable values of V_m for both morpholine and piperidine, the sum totals of δH + δp for morpholine and piperidine are 10.47 and 7.08, respectively, showing that morpholine has a greater ability to swell cotton fiber than has piperidine. Nonpolar interactions between the reagents and cotton fibers may also play some part in the swelling reaction.

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