

Dielectric and Infrared Study of Some Cellulose Derivatives

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Synopsis

Measurements of the dielectric constant of cotton cellulose, mercerized cellulose, cellulose acetate, methyl cellulose, and carboxymethyl cellulose have been carried out in the temperature range of 0–70°C at different frequencies. The results showed that the values of the dielectric constant, with all cellulose derivatives at a given frequency, are greater than that of cotton cellulose and lower than that of mercerized cellulose. The variation of the dielectric constant with temperature showed a transition at 30–40°C with all the samples studied. These results, together with those from infrared spectra and specific volume measurements, indicated that the dielectric behavior depends greatly on the nature of the side group, the degree of hydrogen bonding between the different chains, and the micropores present in the fiber.

INTRODUCTION

Two types of transition have been observed in polymers: the melting or first-order transition and glassy or second-order transition. Cellulose esters,^{1–4} namely, cellulose acetate and butyrates, exhibit two second-order transitions at 30–40°C and at 105–120°C; only the latter transition temperature is lowered by plasticizer. It is probably that the thermal transition of cellulose at about 25°C, as found by different measurement,^{5–15} corresponds to the second-order, low temperature of cellulose esters. The results reported from specific volume¹⁶ and infrared spectra¹⁷ indicate that this transition is a property of hydrogen bonding. The increase of temperature above the transition point leads to the breaking of some weak hydrogen bonds in dry material, thus allowing a greater freedom of some OH groups.

Since the dielectric properties of cellulose depend on the free OH groups, it seemed worthwhile in this investigation to study the dielectric properties of some cellulose derivatives and to correlate the results with those obtained with cotton cellulose and mercerized cellulose. Additional measurements of infrared spectroscopy have been carried out.

EXPERIMENTAL

Materials

Cotton Cellulose. The same as that previously used.¹⁰

Mercerized Cotton Cellulose. It was prepared by steeping cotton cellulose

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in 17.5% NaOH for 75 min, washing with water, steeping in dilute HCl for 30 min, washing with water, and then drying at 60°C.

Cellulose Derivatives. Cellulose acetate, methyl cellulose, and carboxymethyl cellulose were from the same batches as used before.¹⁴

Dielectric Measurements

The equipment used previously¹⁸ in the dielectric measurements was used in this study. It consists of (i) multi-Dekameter, WTW Type DK06, having a frequency range from 0.1 to 12 Mc/sec; (ii) a working cell, Type MFM 5T measuring cell. The cell was modified for dielectric measurements of the test sample under vacuum. The modification made it possible to evacuate the upper part of the cell, in which the test sample was placed, to 10^{-3} mm Hg. The sample was dried at 60°C for at least 8 hr before any measurements.

Infrared Absorption Measurements

Spectra of cotton cellulose, mercerized cellulose, cellulose acetate, methyl cellulose, and carboxymethyl cellulose were obtained in the region from 2 to 4 μm under identical conditions, using the technique of O'Connor et al.¹⁹ The apparatus used was a Perkin-Elmer spectrophotometer Model 337.

RESULTS AND DISCUSSION

The variations with temperature of the dielectric constant ϵ at different frequencies for cotton cellulose, mercerized cellulose, cellulose acetate, methyl cellulose, and carboxymethyl cellulose are shown in Figures 1-5. In Figure 6, the dielectric constant at 2 Mc/sec is plotted against temperature for the above samples.

The results as shown in these figures indicate that (i) The dielectric constant values obtained with all cellulose derivatives at a given frequency are greater than cotton cellulose and lower than mercerized cellulose. (ii) The change of ϵ with temperature is approximately the same for all frequencies. (iii) There is a transition temperature between 30° and 40°C with all the samples studied. (iv) The first four samples show a decrease of the thermal coefficient of dielectric, $d\epsilon/dT$, above the transition temperature, whereas carboxymethyl cellulose shows an increase of $d\epsilon/dT$ above the transition point.

It was pointed out by different investigators¹⁸⁻²² that a decrease in crystallinity is accompanied by an increase in the dielectric constant. This can be explained by assuming that the dielectric constant of cellulose is that of a two-component system: the ordered and the disordered fraction. The latter fraction contains the accessible OH groups responsible for the dielectric behavior. A decrease in the degree of crystallinity or an extension and formation of disordered regions in the crystalline cellulose results in an increased freedom of movement of the OH groups and portions of the cellulose molecule. This is because in the disordered regions the dipolar or molecular polarization is influenced by the proximity and configuration of adjacent molecules; consequently, a decrease in crystallinity results in a greater chance for the disordered chain to achieve random disorder and, therefore, a higher dielectric constant results. On the other

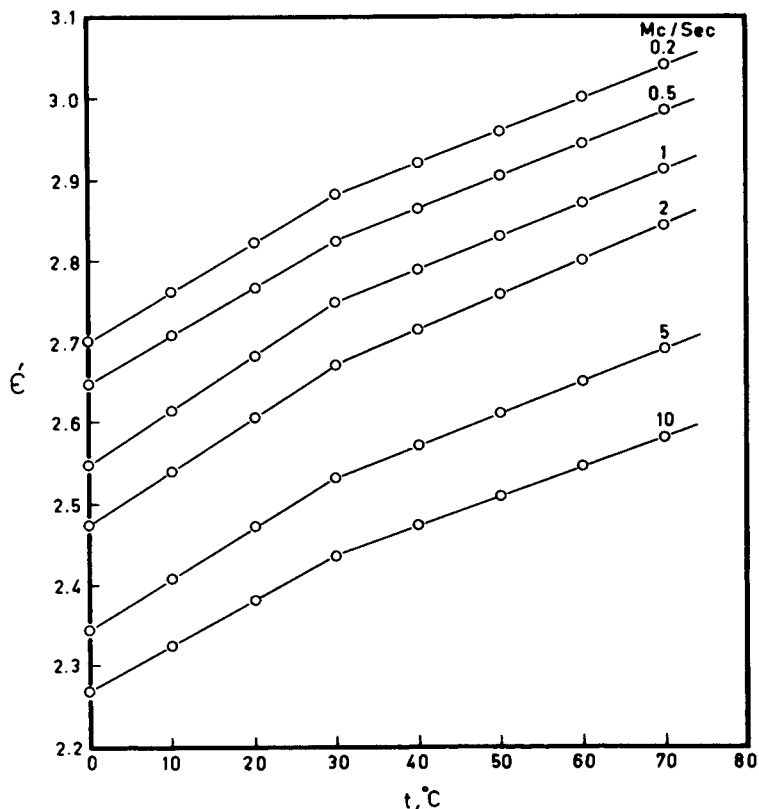


Fig. 1. Variation of dielectric constant ϵ' with temperature, for cotton cellulose at different frequencies.

hand, an increase in the degree of hydrogen bonding between the chains or a blocking of the free OH groups by a substituent group of less polar character would hinder the absorption and, therefore, a decrease in ϵ' occurs.

In view of the above explanation, the higher dielectric constant obtained with cellulose derivatives compared with cotton cellulose, in spite of the partial blocking of cellulose free OH groups by acetyl, methyl, or carboxymethyl group, may indicate a decrease or a weakening of the degree of hydrogen bonding between different chains. The latter may be attributed to the changes that take place in the fine structure of cellulose fiber during the preparation of these derivatives.

Certain areas of the fiber are not accessible to most reagents unless these regions are opened by some kind of pretreatment. Various pretreating agents and conditions are known to influence the reactivity of cellulose by penetration into intermicellar and intramicellar spaces of the cellulose chains. Thus, to facilitate the access of agents and complete the reaction within reasonable time, esterification or methylation is allowed to take place in the presence of swelling agents, such as mineral acids or certain salts. Under such conditions, however, cellulose becomes considerably degraded, particularly if the reaction is allowed to take place at elevated temperature. Therefore, a cellulose derivative may contain a mixture of molecules of greater and smaller chain length, among which esters

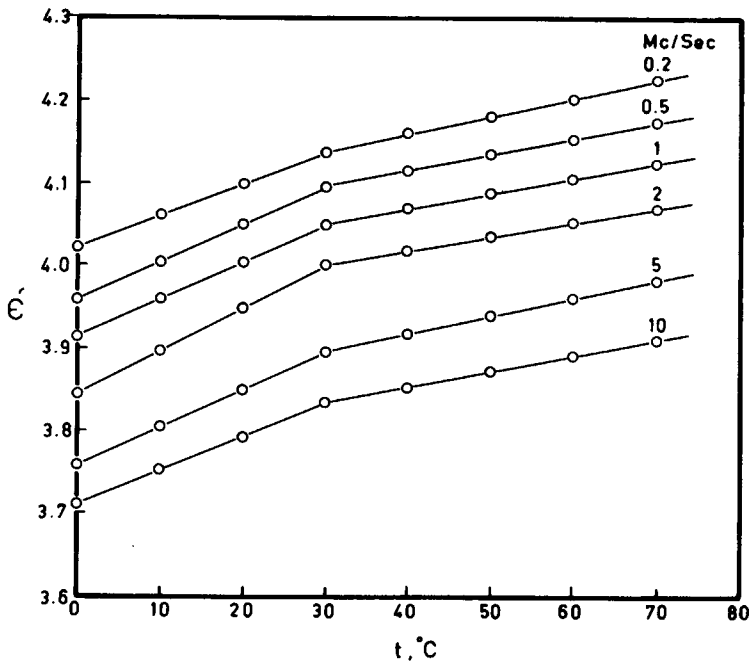


Fig. 2. Variation of dielectric constant ϵ' with temperature, t for mercerized cellulose at different frequencies.

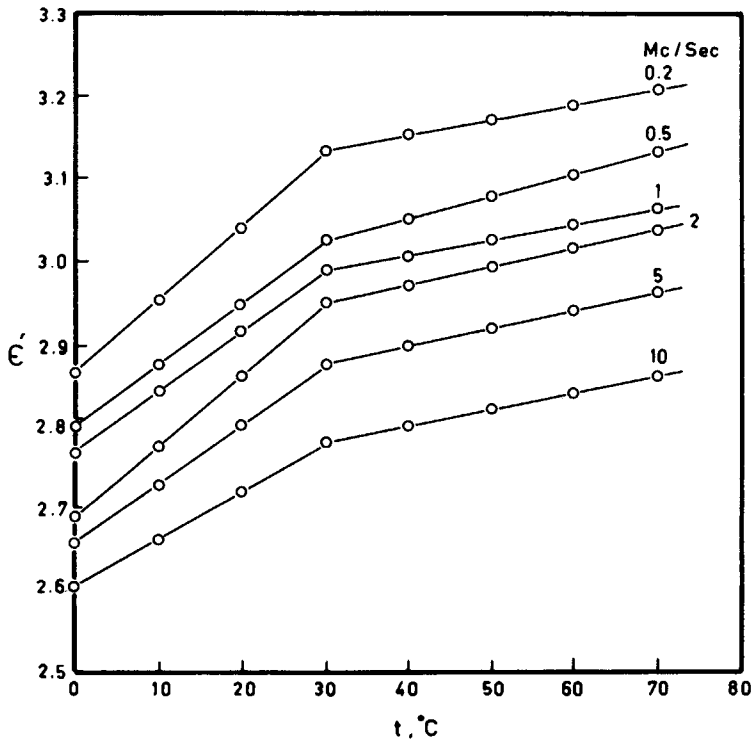


Fig. 3. Variation of dielectric constant ϵ' with temperature t for cellulose acetate at different frequencies.

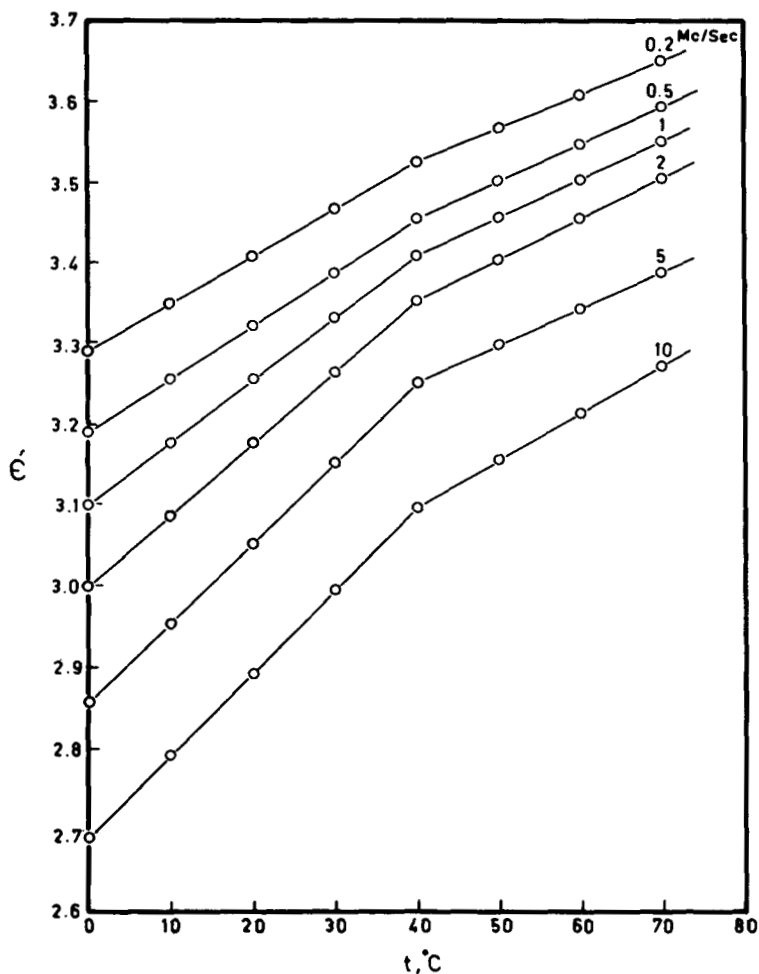


Fig. 4. Variation of dielectric constant ϵ' with temperature t for methyl cellulose at different frequencies.

and ethers even of oligosaccharides, cellobiose and glucose may be found. Thus, all distinction between the regions of varying crystallinity of cellulose fiber is lost due to the destruction of hydrogen bonds between chain molecules as shown by infrared spectra.

For cellulosic substances, the group responsible for the hydrogen bonding is the OH group. Several infrared investigations have been carried out on this subject.^{19,23-28}

The spectra of the different samples obtained in the present work showed that the original band of the OH stretching vibration occurs at 3400 cm^{-1} . As a result of acetylation, methylation, and carboxymethylation, a shift in the same band to a new position of 3480 , 3475 , and 3450 cm^{-1} , respectively, takes place.

When a hydrogen bond is formed between a hydroxyl group and a neighboring oxygen atom, the bond length of the OH increases and the force constant decreases.²⁹ That is to say, acetylation, methylation, and carboxymethylation of cotton cellulose result in a weakening of the degree of hydrogen bonding with a

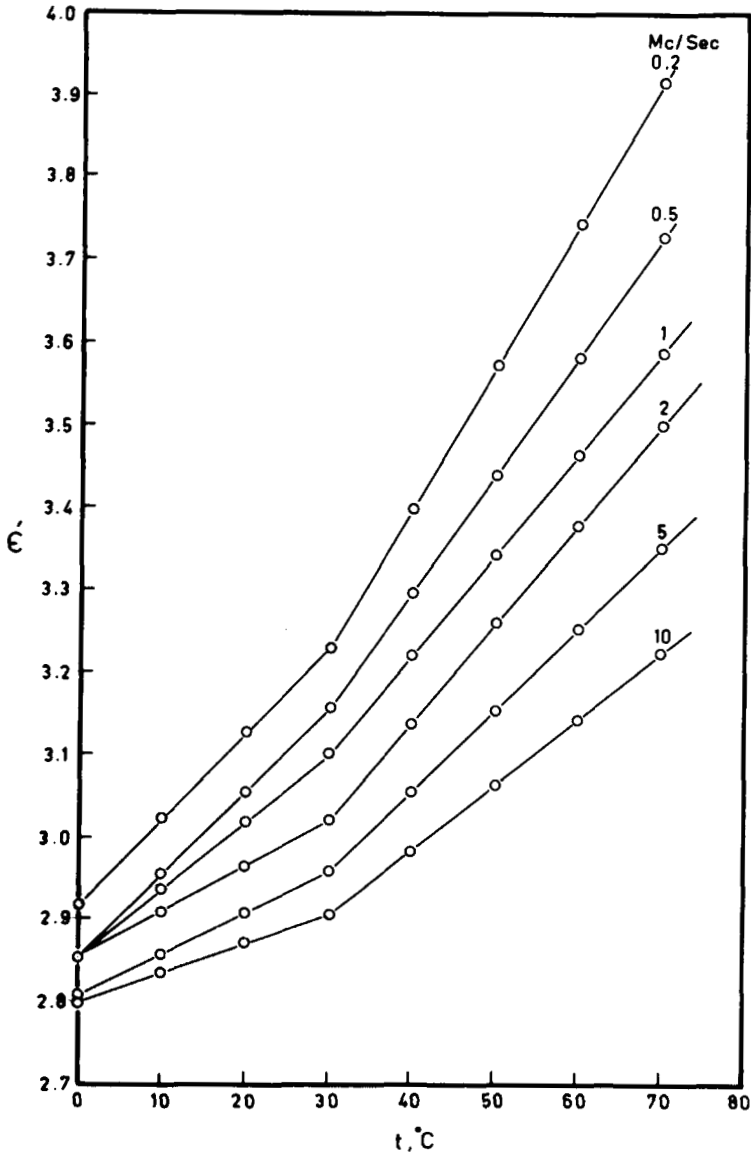


Fig. 5. Variation of dielectric constant ϵ' with temperature t for carboxy methyl cellulose at different frequencies.

consequent shift of the OH stretching vibration bond to a higher frequency. It seems probable that during the preparation of cellulose derivatives the reactions involve the disordered regions of the fiber and remove a greater proportion of the relatively highly hydrogen-bonded OH groups. In addition, the introduction of an acetyl, methyl, or carboxymethyl group may make some initially inaccessible material accessible by propping open the fine structure of the fiber.

Thus, in spite of the blocking action of an acetyl, methyl, or carboxymethyl group, the polarization of cellulose derivatives increases; this may be due to the stabilization of a more open structure which leads to a greater movement of the

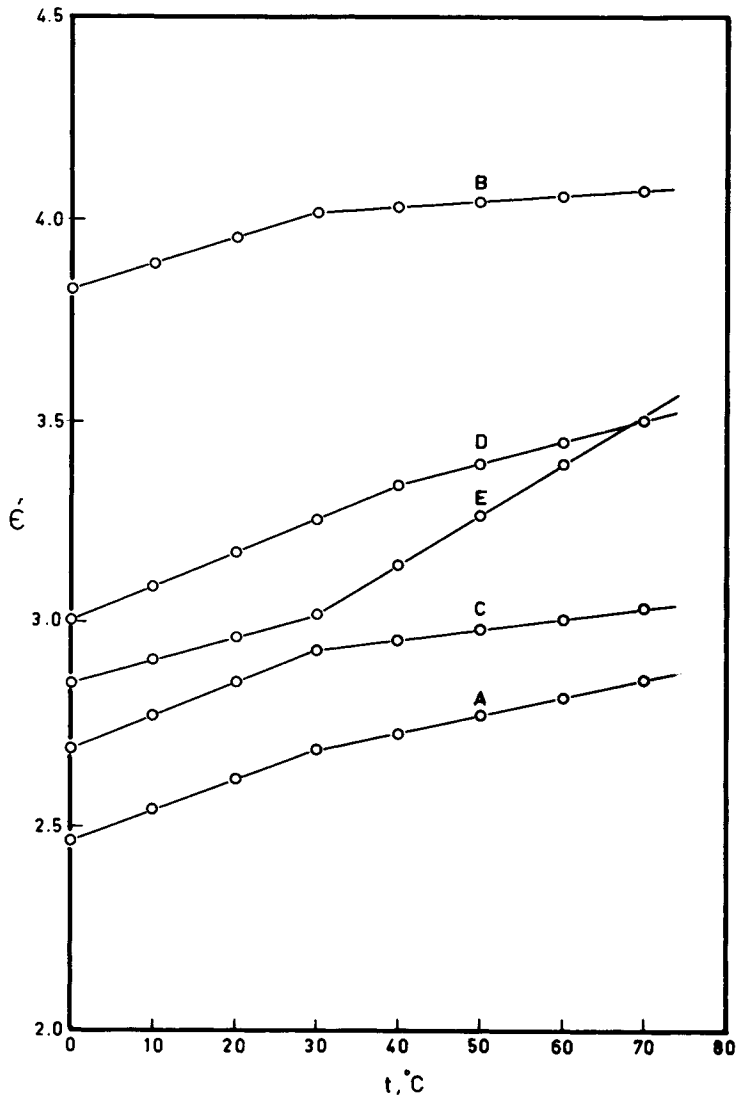


Fig. 6. Variation of dielectric constant ϵ' with temperature t for (A) cotton cellulose, (B) mercerized, (C) cellulose acetate, (D) methyl cellulose, and (E) carboxymethyl cellulose at 2 Mc/sec.

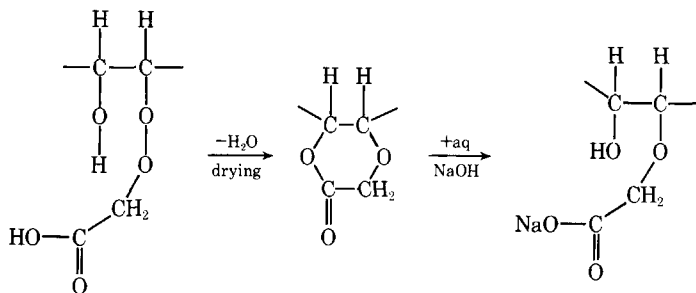
side groups and cellulose chain, resulting in a higher dielectric constant than that of cotton cellulose.

Furthermore, the highest dielectric constant obtained with mercerized cellulose would be expected. Since mercerization leads to the destruction of the highly hydrogen-bonded regions, a shift in the OH stretching vibration band from 3400 to 3450 cm^{-1} was recorded in the present work when cellulose I was converted to cellulose II. Thus, the formation in mercerized cellulose of hydrogen bonds weaker than those of cotton cellulose and the presence of more OH groups in the free state compared with cellulose derivatives lead to the highest dielectric constant independent of the frequency (see Figs. 1-6).

Carboxymethyl cellulose (D.S. = 0.6) is expected to give a higher dielectric

constant than methyl cellulose (D.S. = 2.0) and a lower one than mercerized cellulose. The results show that ϵ for the former derivative is slightly lower than the latter derivative, and it is lower than mercerized cellulose.

Cellulose derivatives, bearing the carboxyl group in the free acid form (such as carboxymethyl and carboxyethyl), are water insoluble; but they become soluble in dilute alkali by forming the alkali metal salt. It would seem that the acid form of the cellulose derivative would also be soluble in water since it would hydrate readily. In order to explain these observations, Chowdhury³⁰ presented the theory that the acid form of cellulose derivative forms a lactone ring with unreacted hydroxyl groups of the cellulose molecule upon drying; this gives an insoluble product. In alkali, the rings are opened yielding the soluble sodium salt:



Thus, the formation of a lactone ring in carboxymethyl cellulose may account for its low dielectric constant. A detailed study on the effect of the degree of substitution of the carboxymethyl group on the dielectric behavior of cellulose before and after treatment with sodium hydroxide will be reported in a subsequent paper.

The observed transition temperature at 30–40°C as shown in Figures 1–6 agrees well with the previous investigations.^{5–15} The results also indicate that, whereas the thermal coefficient of the dielectric, $d\epsilon/dT$, increases above the transition temperature for carboxymethyl cellulose, it decreases with the other cellulosic samples studied.

The specific volume results obtained previously^{10,14} indicate that the thermal coefficient of expansion, λ , of all the samples investigated increases above the transition temperature. The latter was attributed to breaking of some weak hydrogen bonds in the dry material, thus allowing a greater freedom of movement of some OH groups. This may result in a greater polarizability, and an increase in $d\epsilon/dT$ above the transition temperature takes place, especially with samples containing more weakly hydrogen-bonded regions. The results obtained for $d\epsilon/dT$ with different samples show that there would be other factors which affect the change of the dielectric constant with temperature above the transition temperature. Thus, to throw more light on the effect of temperature on the polarizability of cellulose and cellulose derivatives, it seemed worthy to analyze the data obtained previously^{10,14} in this laboratory with the same samples.

Table I includes the values of λ before and after the transition temperature. The ratio λ_a/λ_b was determined, and the values are cited in the last column.

The values of λ presented in Table I involve the temperature coefficient of expansion of both ordered and disordered regions which may differ owing to the presence of impenetrable micropores in the latter regions. While that of the

TABLE I
Apparent Thermal Coefficient of Expansion (λ)
of Some Cellulosic Materials in Toluene

Material	Apparent thermal coefficient of expansion ($\lambda \times 10^5 a$)		$\lambda_a \lambda_b$
	Below transition temperature (λ_b)	Above transition temperature (λ_a)	
	Cotton cellulose	6.0	
Mercerized cellulose	4.4	5.8	1.32
Cellulose acetate	18.0	24.0	1.35
Methyl cellulose	19.0	26.0	1.37
Carboxymethyl cellulose	9.0	15.0	1.66

^a In toluene.

ordered regions should not vary appreciably with the buoyancy medium as in the case of cellobiose,¹⁰ the apparent thermal expansion of the disordered regions will depend on the extent of penetration of the displacement medium at different temperatures.

There are two factors which affect the value of λ in opposite directions: the thermal expansion of the pores, which are inaccessible for molecules, of the buoyancy liquid tends to increase the value of λ ; on the other hand, if the pore width is comparable with the volume of the liquid molecules, then the thermal expansion of these pores may allow penetration of liquid at a higher temperature which tends to decrease λ . If we consider that the expansion of the impenetrable micropores is nearly the same before and after the transition temperature, and that the penetration of the displacement medium with increasing temperature tends to decrease λ , a value of the ratio $\lambda_a | \lambda_b$ higher than unity would result only if a greater movement of the free weakly hydrogen-bonded OH groups occurs. This ratio may be taken as a measure of the sum of the different changes that take place above the transition temperature. The results in Table I indicate that carboxymethyl cellulose show the highest value for $\lambda_a | \lambda_b$ compared with the other samples studied, which have nearly the same ratio $\lambda_a | \lambda_b$.

In view of the above explanation, one may expect that mercerized cellulose would have the highest $\lambda_a | \lambda_b$ value; this does not agree with the practical results. Therefore, we may conclude that although mercerized cellulose possesses a great disorder of arrangements of cellulose chain in the accessible regions, the arrangement of chain molecules does not seem to allow greater movement of the OH groups above the transition temperature. Accordingly, the change of the thermal coefficient of a certain characteristic property of a cellulose substance above the transition temperature depends not only on the free OH groups and the hydrogen bonding between these groups, but also on the interchain spaces between cellulose chains. Thus, the decrease of $d\epsilon/dT$ as obtained with mercerized cellulose and all cellulose derivatives investigated, except carboxymethyl cellulose, above the transition temperature may be due to greater bulkiness of the side groups which hinders the polarizability of these side groups and flexible portions of cellulose molecules.

On the other hand, the lactone ring formation in carboxymethyl cellulose seems

to provide interchain spaces which expand with increasing temperature and show no hindrance effect; this results in a high polarizability above the transition temperature and an increase in $d\epsilon/dT$.

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