

# Dielectric Spectroscopy and Relaxation Phenomena of Moistened and Dry Polysaccharides

H. G. Shinouda, M. M. Abdel Moteleb

Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt

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**ABSTRACT:** The effect of hydration on the dielectric constant  $\epsilon'$  and loss factor  $\tan \delta$  of viscose hydrocellulose, hydroxypropyl cellulose, and dextran was studied in a wide range of temperatures and frequencies. The results obtained reveal that (1) whereas hydration shows little effect on the variation with temperature of both  $\epsilon'$  and  $\tan \delta$  of hydrocellulose, the presence of adsorbed water significantly modifies the dielectric behavior of the other two samples; (2) only one relaxation denoted as  $\gamma$ -process is observed in the case of hydrocellulose sample irrespective of its moisture content; (3) two absorption peaks are recorded with moistened hydroxypropyl cellulose and dextran specimens, one below room temperature denoted as  $\beta$ -process and a dispersion loss at high temperature; and (4) after drying of these sam-

ples, the dispersion loss peak disappears, the  $\beta$ -peak diminishes, and the  $\gamma$ -peak, which is hidden behind the sizable  $\beta$ -peak, is observed and that, although with increasing frequency, the former peak disappears, the intensity of the latter one increases. The analysis of these results in view of the chemical and the fine structure of the test samples as well as the calculated activation energy indicates that the  $\gamma$ - and  $\beta$ -relaxations recorded are of different natures. The satisfactory interpretation given clarifies to a great extent the contradictions reported in the literature concerning the relaxation phenomena in polysaccharides. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 571–582, 2005

**Key words:** dielectric properties; polysaccharides; relaxation

## INTRODUCTION

The chemical and physical behavior of the complex structure of the polysaccharide–water system is greatly dependent not only on the amount of water present but also on the mode of interaction between the polymer chains and water molecules, which may change by changing the drying condition used in the different investigations.<sup>1–7</sup> Accordingly, the results obtained and the interpretation given by different authors using various techniques<sup>8–41</sup> to study the relaxation phenomena of polysaccharides and related compounds do not agree about the origin of the molecular dynamics of the observed relaxations and there still many open questions about the origin of such relaxations. Therefore, the present work has been undertaken to study the dielectric behavior of some celluloses and dextran of different water contents, fine structure, polarity, and glucosidic linkage by measurements of both real and imaginary parts of the complex dielectric in a wide range of temperatures and frequencies.

## EXPERIMENTAL

### Materials

Polysaccharides of different moisture contents, fine structure, polarity, and glucosic linkage were used to study the effect of these parameters on the dielectric properties of these hygroscopic materials. To attain this purpose, three different types of polysaccharides, namely, viscose hydrocellulose, hydroxypropyl cellulose, and dextran, were used. Following are some of the characteristic properties of these materials.

### Viscose hydrocellulose residue

Viscose hydrocellulose residue was prepared from viscose rayon (Cairo, Egypt), as before,<sup>42</sup> in which the fibers were subjected to acid action by using 1N HCl at 100°C for 10 h in which a ratio of 1 : 50 viscose-to-acid was used; the powder obtained was washed with water until free from acid. The characteristic properties of the hydrolysis residues were previously studied in our laboratory.<sup>43–45</sup> The sample prepared is of average degree of polymerization, of 38, and of X-ray crystallinity index,  $Cr_x = 70$ , determined by using the procedure of Segal et al.<sup>46</sup>

### Hydroxypropyl cellulose

Hydroxypropyl cellulose (Kucel E) was provided by Hercules (Hercules Chemical, Wilmington, DE). This

Correspondence to: H. G. Shinouda (Hakimshinouda@hotmail.com).

sample is of weight-average molecular mass,  $M_w = 80,000$ , and molecular substitution,  $MS = 3.0$ . In addition, determined X-ray diffraction showed a diffuse X-ray pattern, indicating that this derivative is of high disordered structure.

### Dextran

Dextran was provided by LTD Chemical (Poole, UK) and characterized by weight-average molecular mass,  $M_w = (60,000-90,000)$ , and the X-ray crystallinity index measured here showed a diffuse pattern as found with hydroxypropyl cellulose.

### Sample preparation

#### Disc-forming of test sample

Test samples were prepared in the form of 30-mm-diameter discs about 0.1- to 0.3-mm-thick by pressing the test sample by hydraulic pressure at 70 mPa.

#### Moistened and dry samples

The following are the steps used to prepare moistened and dry samples for dielectric measurements.

#### Moistened samples

Two air-conditioning samples, referred to as moistened samples, were prepared as solid discs and subjected to air moisture at room temperature. One of the two samples was used to determine its moisture content gravimetrically by weighing the sample before and after heating at 110°C for 4 h. The percentages of moisture contents obtained are 8.0, 6.0, and 13.0 for hydrocellulose, hydroxypropyl cellulose, and dextran, respectively. The second sample was used for dielectric measurements: first, by cooling the sample to -160°C, and then, a dielectric scan was recorded during heating the sample from -150 to 110°C. The detailed procedure is shown later.

#### Dry samples

Dry samples were prepared by heating the moistened sample while enclosed in the measuring dielectric cell. The heating and measurement system will be described in the following section. To attain the best condition for drying, the effect of time on  $\epsilon$  of the test sample was followed after the temperature of the sample reached 110°C. This was carried out with increasing time of heating while the temperature is kept constant at 110°C and the dielectric constant was recorded at different intervals until a constant  $\epsilon$  value was attained that hardly showed any further change with time. The time required to reach such a constant

$\epsilon$  value was found to be at least 180 min and increased to 240 min depending on the hygroscopic nature of the sample under test. These samples will be referred to as dry samples, although it is expected that they still retained some residual water. Such dry samples while enclosed in the dielectric cell was allowed to the desired dielectric measurements and the results will be compared with the results obtained with those of the moistened samples.

### Heating and measurement systems

Heating and measurement systems operate fully automated under the control of a PC with the MS.WINDOWS™ software package winDETA supporting the independent variables of frequency, temperature, and time. These three variables can be arranged in arbitrary order. The results are graphically displayed in two-dimensional diagrams. Diagrams are pointed with high resolution on any pointer supported by MS.WINDOWS™ and can be expanded into other programs. Data are saved either as ASCII tables or as binary files in variable forms.

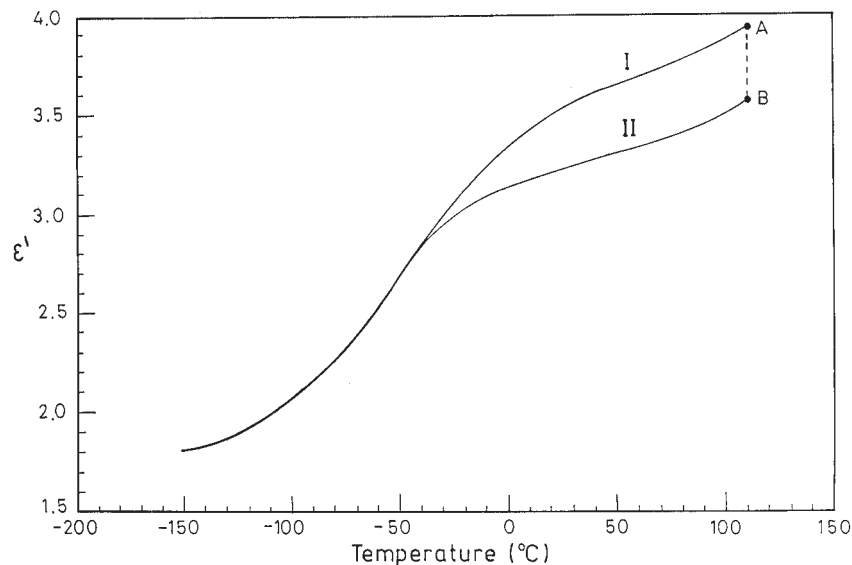
### Dielectric measurements

The dielectric constant,  $\epsilon$ , and dielectric loss factor,  $\tan \delta$ , were measured by using BDS 1200 cell connected to impedance Analyzer Hewlett-Packard 4284 for frequencies from 20 Hz to 1M Hz with a resolution in loss factor  $\tan \delta < 0.5$  mrad. Samples were cooled or heated in an ascending or descending order at a rate of 1°C/min by adjusting the automated system as stated above. Such slow rate was chosen to allow the sample as much as possible to thermal equilibrium during measurements. The dielectric spectroscopy scan for the change of  $\epsilon$  as well as the loss factor  $\tan \delta$  as a function of temperature was recorded at different frequencies. Two subsequent scans for each sample examined were carried out: one scan was performed for the moistened sample before drying, first by cooling the sample to -160°C; then, the results were recorded by increasing the temperature in ascending order until the temperature reached 110°C. The second scan was recorded after drying was achieved, and then the temperature was decreased in a descending order from 110 to -150°C.

## RESULTS AND DISCUSSION

### Water-desorption and dielectric function, $\epsilon(t)$

To get more insight into the changes in the inter- as well as the intramolecular interaction that occur as a result of desorption of water accompanying thermal treatment, it seems worthy to follow such changes by following the variation with temperature of the dielec-

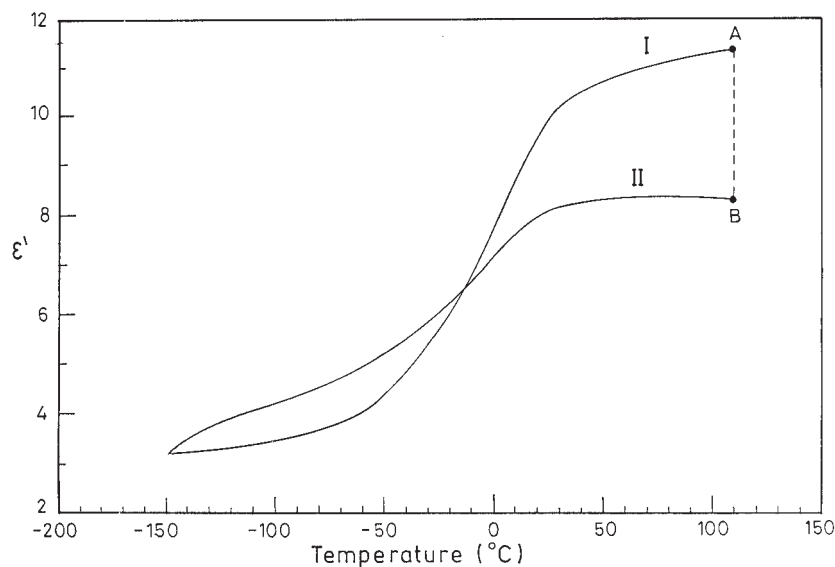


**Figure 1** Variation with temperature of the dielectric constant,  $\epsilon'$ , of viscose hydrocellulose (I) moistened sample and (II) dry sample.

tric constant,  $\epsilon$ . This was performed by recording  $\epsilon$  during heating the moistened sample from  $-150$  to  $110^\circ\text{C}$ , and then during heating the sample at a constant temperature,  $110^\circ\text{C}$  for different time intervals until  $\epsilon$  attains a constant value, and finally, during cooling the resulting dry sample from  $110$  to  $-150^\circ\text{C}$ .

The results obtained for the variation of  $\epsilon$  with temperature are shown in Figures 1, 2, and 3 for viscose hydrocellulose, hydroxypropyl cellulose, and dextran, respectively, where curve (I) in each figure represents the results of the moistened sample and curve (II) represents the dry specimen. These results in

general reveal that there is a significant difference between the change with temperature of  $\epsilon$  for each sample before and after drying as well as among the examined samples whether moistened or dry. While hydrocellulose residue before and after drying shows the lowest  $\epsilon$  values compared with the other two test samples throughout the whole temperature range, hydroxypropyl cellulose gives the highest values. Furthermore, Figure 1 shows that  $\epsilon$  of viscose hydrocellulose sample below  $-30^\circ\text{C}$  is the same for both moistened and dry specimens and with increasing temperature  $\epsilon$  increases. This increase is slightly



**Figure 2** Variation with temperature of the dielectric constant,  $\epsilon'$ , of hydroxypropyl cellulose (I) moistened sample and (II) dry sample.

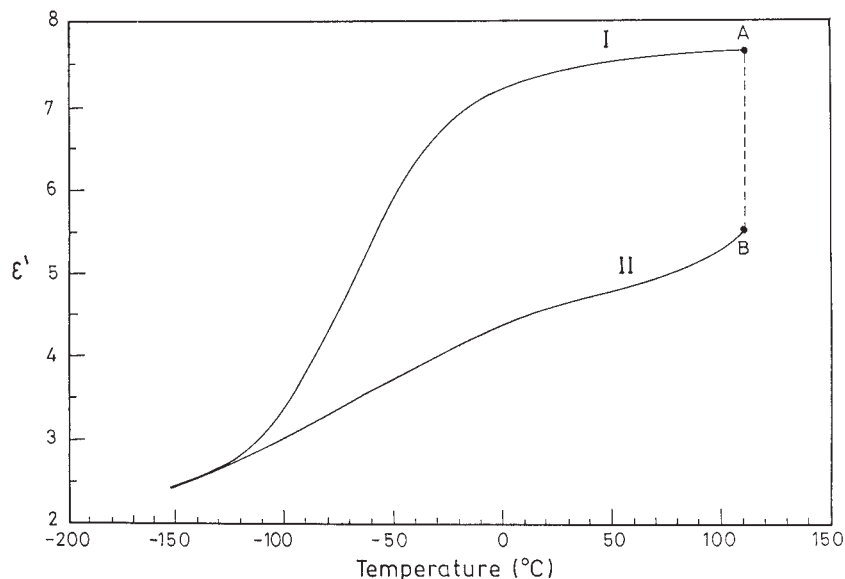


Figure 3 Variation with temperature of the dielectric constant,  $\epsilon'$ , of dextran (I) moistened sample and (II) dry sample.

higher in the case of moistened sample than that for a dry sample. In the case of hydroxypropyl cellulose, it is evident from Figure 2 that  $\epsilon'$  in the low temperature range is higher for the dry sample than the moistened one and at higher temperature the reverse occurs. With dextran as given in Figure 3, the results show that  $\epsilon'$  of moistened sample is higher than the dry sample throughout the whole temperature range.

The effect of water on the dielectric polarization of cellulosic materials was previously studied.<sup>26-28</sup> The reported results indicate that the mobility and hence the alignment of molecular chains in the disordered regions of polysaccharides, responsible for dielectric polarization, depend not only on the amount of water present but also on the mode of interaction between water molecules and cellulose chains. Also, it has been found<sup>1,2</sup> that, during thermal treatment, the removal of water molecules from the disordered regions results in some changes in the intermolecular interaction between adjacent cellulose chains. Furthermore, in view of the sorption-desorption behavior, it has been pointed out<sup>47</sup> that once the less-difficult accessible regions of the polymer are disrupted by swelling, the water molecules adsorbed in the inner fine structure would be the last to leave upon decreasing the vapor pressure. Accordingly, it has been presumed<sup>12,48</sup> that, after vigorous drying of cellulosic materials in air, it is expected that some residual water, most probably, is still retained in the inner fine structure of the resulting dry sample.

To analyze the present results, one has to take into consideration the above findings as well as the difference in the chemical as well as the fine structure of the examined samples as given by X-ray crystallinity index obtained here and those previously reported by

using different methods.<sup>12,42-45,48,49</sup> The outcome of these results shows that, on the contrary to hydroxypropyl cellulose and dextran of completely amorphous structure, viscose hydrocellulose residue is of high X-ray crystallinity index amounting to 70%. This high-crystallinity value is a result of the change in crystallinity of viscose fibers from 40 to 70% due to acid hydrolysis. It has been reported<sup>42,45</sup> that this increase in crystallinity that takes place in the initial stages of hydrolysis is due to the following: (1) the dissolution of highly disordered regions and the destruction microcapillaries originally present in viscose fibers and (2) the tight packing of the original semicrystalline regions in the fibers as well as the aggregation of the different particles, which split off during hydrolysis through strong hydrogen bonding, forming crystallites that could be detected by X-ray diffraction. On prolonged acid action, more aggregation of small particles takes place in the late hydrolysis residue through strong hydrogen bonds forming new disordered regions rich in micropores inaccessible to organic liquids. After the fibers have suffered 1-4% dissolution, the resulting residue is composed of a mixture of particles of various lateral orders of arrangement, of lower degree of polymerization, and of lower heat of wetting compared with the original viscose fibers. In the present work, the hydrocellulose sample prepared is of degree of polymerization, amounting to 38, and of a leveling-off constant heat-of-wetting value amounting to about 70% of that of the original unhydrolyzed fibers. Based on these results, it has been concluded that in these residues adsorption of water takes place in fewer layers than in the original fibers and would be under a stronger influence of cellulose surface. In addition, a compari-

son between their crystallinity determined by X-ray and iodine adsorption method led to a conclusion that these rigid residues are of high surface area and that adsorption of iodine molecules takes place mainly on their surface. In view of these findings together with Herman's statement<sup>50</sup> that in cellulosic fibers there are certain points of contact between molecular chains where cohesion is such that cellulose-to-cellulose bonds could not be perturbed by water, dyestuffs, or iodine molecules, one may conclude that in the case of the moistened hydrocellulose sample of moderate moisture contents of 8% as found in this investigation, adsorption of water from ambient takes place most probably on the surface of this rigid sample.

Therefore, the similar changes of  $\epsilon$  with temperature of moistened and dry hydrocellulose sample during thermal treatment at low temperature and the slight change that occurs at higher temperature and after their vigorous drying at 110°C could be attributed to the following: (1) the mode of interaction with cellulose molecules of the adsorbed water that takes place mainly on the surface of these residue has little effect on its dielectric polarization and that (2) during thermal treatment and before the temperature reaches 110°C most of the surface sorbed water evaporates and that the residual amount of water confined in its fine structure which desorbed on drying the sample at this temperature is very small. In accordance with this is the relatively high amount of easily cycled sorption-desorption of water (when the sample is repeatedly remoisturized and dried) amounting to 8% in the case of this sample compared with those of the completely amorphous hydroxypropyl cellulose and dextran samples, amounting to 6 and 13%, respectively. These amounts of humidity adsorbed from ambient were found to be almost the same when the sample cycled to dryness and cooled and then remoisturized. The relatively high accessible sites of hydrocellulose sample to water adsorption as stated above is due to the increase of their surface area and that is why most of the adsorbed water is easily evaporated on thermal treatment. Hence, one may add that the drying procedure utilized here is very efficient and that the rigid dry hydrocellulose sample used in this work could be considered as a true dry sample.

In the case of the highly disordered structure hydroxypropyl cellulose derivative, the glucose rings with  $\beta(1-4)$ -glucosidic linkage are functionalized by the bulky side-chain hydroxypropyl groups. It has been postulated<sup>49</sup> that this material has a relatively rigid backbone to which flexible side groups are attached. It is expected that this derivative with a different dipole moment and conformation mobilities would give different dielectric results when compared with the other two test samples. The results as shown in Figure 2 imply that, despite the blocking action of the hydroxypropyl side group and the low moisture

contents of 6%, the dielectric polarization throughout the whole temperature range is much higher than hydrocellulose sample. This could be mainly due to several changes that take place during the preparation of this derivative. The most important of these changes in the resulting derivative are the high disordered structure as well as the more flexible side group and in turn the expected weakening in the degree of hydrogen bonding. Similar results that cellulose derivatives show higher  $\epsilon$  than unsubstituted cellulose have been previously reported with some cellulose derivative.<sup>51</sup> With increasing temperature and desorption of water from this moistened sample, the changes in the inner fine structure accompanying these processes leads to a pronounced increase in polarization. This implies that after desorption of water molecules the change of the inter- as well as the intramolecular forces taking place decreases. Also, in the case of dextran desorption of water by heating, the moistened sample is accompanied by increased polarization. However, the shape and extent of the observed change is different when compared with the other two samples. This could be understood if one takes into consideration that this sample is of different fine structure, as evidenced by its high adsorption capacity to water amounting to 13.0%, and that it has three secondary hydroxyl groups and a more flexible  $\alpha(1-6)$ -glucosidic linkage.<sup>12,17</sup>

When the samples were heated at 110°C for a long period, most of the sorbed water evaporates, leading to some changes in the inter- as well as intramolecular interaction by the formation of new junctions either between cellulose chains or between these chains and any residual water if present. The dielectric polarization which is dependent on the concentration and mobility of the polar groups of cellulose chains in the amorphous regions of each sample are modified, resulting in a drop in  $\epsilon$  from point A on curve (I) to point B on curve (II). From the drop of  $\epsilon$  as observed in Figures 1-3, the percentage decrease of  $\epsilon$  (from A to B) for the test samples was calculated and has been found to be 28.0, 26.0, and 12.8 for dextran, hydroxypropyl cellulose, and hydrocellulose, respectively, which indicates that such decrease takes place in descending order: dextran > hydroxypropyl cellulose > hydrocellulose. This decrease in polarization after drying may be a result of the following two combined effects: (1) the desorption of water molecules that are strongly hydrogen bonded with the disordered regions responsible for the high polarization observed with the moistened samples; and (2) the mode of interaction that takes place between the polymer chains in the disordered regions after water desorption. The observed lower decrease of dielectric polarization in the case of hydrocellulose sample compared with the other two samples is to be expected because of the lack of this residue to highly disordered



regions responsible for such changes compared to the other samples. Furthermore, one may add that most of the adsorbed water evaporates from this sample during its thermal treatment until the temperature reached 110°C and that the low value of the percent decrease of  $\epsilon$  as a result of heating the sample for a long period at this temperature indicates that almost no residual water is retained by this sample after drying and in turn the inner fine structure of this rigid residue is inaccessible to water molecules, which confirms the conclusion drawn above that this residue after drying is free of water. On the contrary, in the case of the two other examined samples, the change of dielectric constant as well as the relatively high percentage decrease of  $\epsilon$  on drying indicate that these samples during different stages of thermal treatment before as well as after 110°C is still expected to possess a relatively small amount of water compared with the viscose hydrocellulose sample.

After drying is achieved, lowering the temperature of the dry sample results in a decrease in the dielectric constant, which differs from one sample to the other and in particular at low temperature. Regarding dry hydrocellulose residue, at temperatures below -30°C, the values of  $\epsilon$  coincide with those of the corresponding moistened sample. These results reveal that drying of this rigid sample has little effect on its dielectric polarization, which is expected because of the absence of an effective amount of adsorbed water in this specimen. On the other hand, hydroxypropyl cellulose shows that in such low temperature range the dielectric constant of dry sample is slightly higher than the corresponding moistened specimen, indicating that desorption of water results in some structural changes, leading to an increased polarization. This could be due to the presence of the bulky chain hydroxypropyl side group, which causes less close packing of cellulose chains, after water desorption, and, hence, the observed high dielectric constant. With dry dextran, desorption of water leads to a remarkable percentage decrease of its dielectric constant, which infers that this sample possesses higher adsorption sites to water than the two other examined samples, agreeing well with the high moisture contents amounting to 13% for the air-conditioning sample. In addition, the results reveal that in this dry sample more increase in its inter- as well as intramolecular forces takes place between polymer chains in the disordered regions. In the absence of bulky side groups in such unsubstituted highly amorphous polysaccharide and after water desorption from its disordered regions, it seems that closer packing of the polymer chains in these regions takes place and thus the mode of interaction occurs between the polymer chain and the change in dielectric polarization that takes place is expected to be different when compared with the changes that occur in the corresponding regions in the

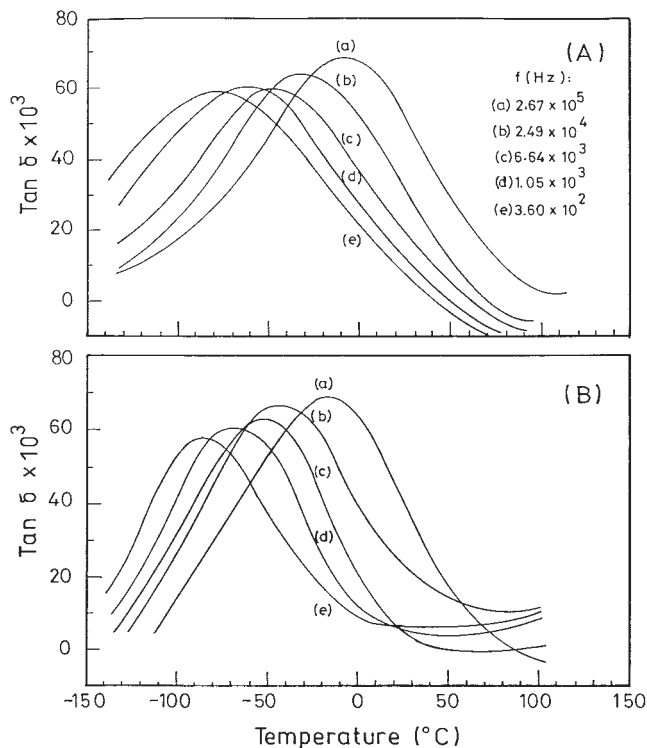


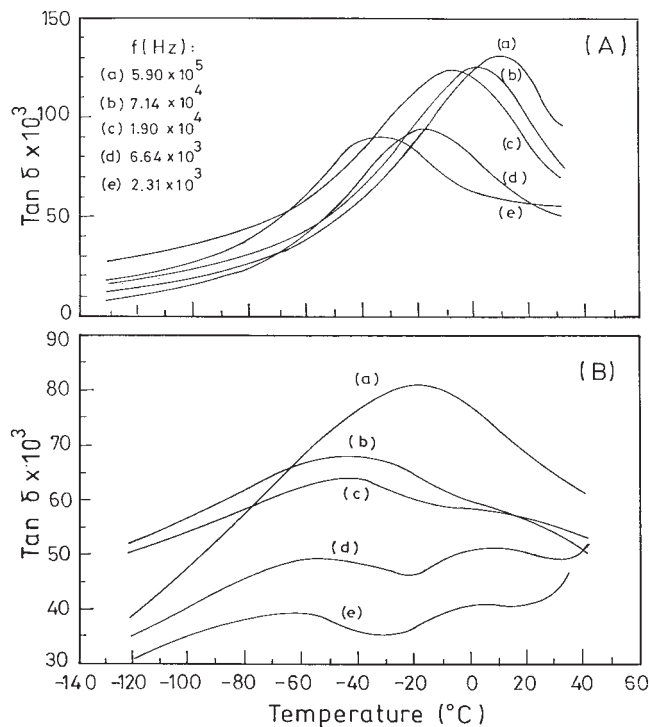
Figure 4 Variation with temperature of  $\tan \delta$  of viscose hydrocellulose (A) moistened sample and (B) dry sample.

two other test samples. Based on these findings, it is evident that, not only the amorphous contents, but also the composition of the sample, play an important role in the sorption and desorption of water, which is reflected on the observed changes of dielectric polarization during thermal treatment.

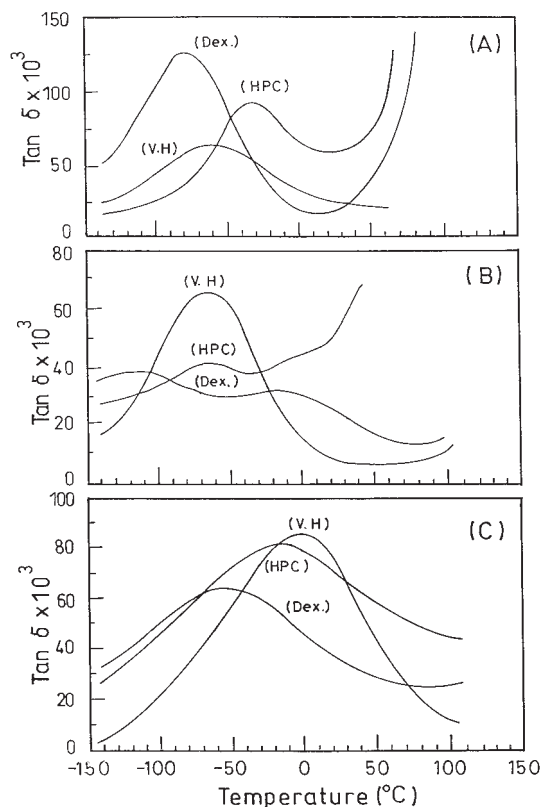
#### Relaxation processes and dielectric loss factor, $\tan \delta$

The variation with temperature of the dielectric loss factor  $\tan \delta$  recorded at different frequencies for moistened and dry samples of hydrocellulose, hydroxypropyl cellulose, and dextran are given in Figures 4-6. For the sake of comparison, Figure 7(A,B) shows the results of moistened and dry samples, respectively, at 1.05 kHz, whereas Figure 7(C) gives the results for the latter samples at a higher frequency of  $5.9 \times 10^2$  kHz. Figure 8 gives the results of the same samples at a low frequency of 280 Hz. In Figures 4-8, the portion of the curves in the vicinity of maximum loss has been displayed for clarity.

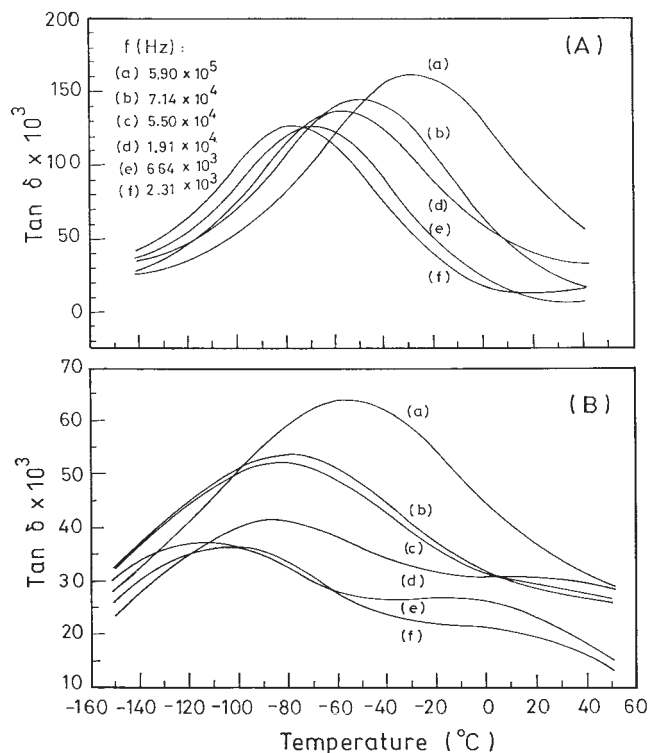
It is obvious from these figures that (1) below room temperature viscose hydrocellulose sample before and after drying shows only one absorption loss peak, slight increases in intensity, and shifts to somewhat lower temperature on drying. This peak is of much lower intensity compared with the intensity of the moistened dextran and hydroxypropyl cellulose sam-



**Figure 5** Variation with temperature of  $\tan \delta$  of hydroxypropyl cellulose (I) moistened sample and (II) dry sample.

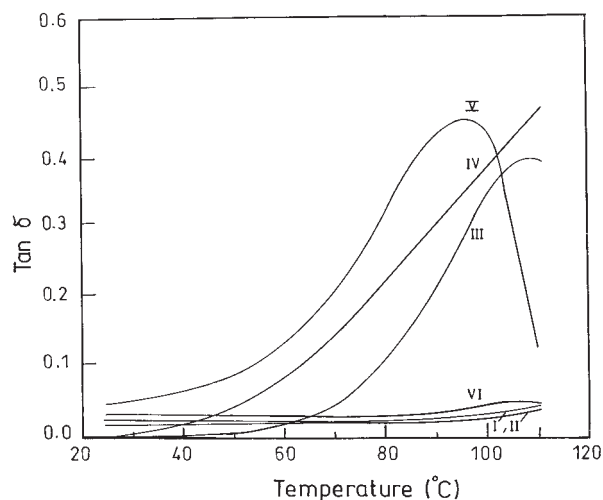


**Figure 7** Variation with temperature of  $\tan \delta$  of viscose hydrocellulose (V.H.), hydroxypropyl cellulose (HPC), and dextran (Dex.): (A) moistened samples at 1.05 KHz, (B) dry samples at 1.05 KHz, and (C) dry samples at  $5.9 \times 10^2$  KHz.



**Figure 6** Variation with temperature of  $\tan \delta$  of dextran (A) moistened sample and (B) dry sample.

ples; (2) moistened hydroxypropyl cellulose and dextran samples containing from 6 to 13% moisture contents exhibit one loss peak below room temperature and a dispersion loss peak at high temperature; (3) the



**Figure 8** Variation with temperature on  $\tan \delta$  at 280 Hz of (I) moistened and (II) dry viscose hydrocellulose, (III) moistened and (IV) dry hydroxypropyl cellulose, (V) moistened and (VI) dry dextran.

TABLE I  
Calculated Energy of Activation,  $\Delta E^*$ , kJ/mol<sup>a</sup>

Sample	Moistened samples	Dry samples
Viscose hydrocellulose	41.0	39.9
Hydroxypropyl cellulose	60.0	40.0
Dextran	39.0	32.0

<sup>a</sup> The error in the calculated values of  $\Delta E^*$  does not exceed  $\pm 3.0\%$ .

shape, the intensity, and the location of the maximum temperature of the low-temperature loss peak are dependent on the moisture contents, test frequency utilized, and the chemical as well as the fine structure of the examined sample; (4) in the case of the corresponding dry samples, two weak absorption peaks are observed below room temperature, in which the sizable loss peak recorded with the corresponding moistened ones is shifted to higher temperature and its intensity decreases swamped with a conduction loss in the case of hydroxypropyl cellulose, and a second absorption loss peak located at lower temperature appears. With increasing frequency, the results reveal that, while the lower temperature loss peak is shifted to higher temperature and its intensity increases, the higher temperature one gradually diminishes, becomes broader, and is expected to vanish if a truly dry sample could be obtained. Above room temperature and at low frequency, Figure 8 shows one dispersion loss peak with the moistened hydroxypropyl and dextran samples, while such a dispersion loss is not recorded either with the corresponding dry samples or with both dry or moistened hydrocellulose residues. Dry hydroxypropyl cellulose shows an increase of  $\tan \delta$  with increasing temperature due to conduction loss.

From the absorption loss data as shown in Figures 4–6, the apparent activation energy,  $\Delta E^*$ , was determined for each sample examined from the slope of the straight line drawn through the points of a plot representing the relation between  $\log$  frequency against the reciprocal of the absolute temperature at which maximum loss occurs. The results obtained are cited in Table I.

These results show that, whereas the value of  $\Delta E^*$  for both moistened and dry hydrocellulose sample is close and similar to that determined with dry hydroxypropyl cellulose, the lower value is found with dry dextran. On the other hand, the activation energy values in the case of moistened hydroxypropyl cellulose and dextran are higher than the values of the corresponding dry samples and that  $\Delta E^*$  for the former specimen is much higher than that of the latter specimen.

To analyze and interpret the above results, consideration should be given to the fact that dielectric spectroscopy, besides recording the magnitude of dielec-

tric polarization, is very sensitive to detect the velocity of orientation changes of dipoles and provides experimental results concerning the mobility of polar regions and dipolar side groups within a small unit in the materials exposed to an electric field. In addition, it has been postulated<sup>52</sup> that, whereas the polarity and in turn the dielectric constant is a measure of the concentration and moments of the dipolar groups along the polymer chain, the observed loss is chiefly governed by the dipole interaction between the adjacent chains, which arises from the formation of dipole layers and is largely independent of polar group concentration. Therefore, inter- as well as intramolecular forces should play an important role in the molecular dynamics for any system under investigation.

As regards the molecular interactions in cellulose-water system, adsorbed water is generally believed to be held to cellulose through hydrogen bonds.<sup>53–58</sup> According to previous authors,<sup>35,57,58</sup> one has to distinguish between different types of water in such a complicated system and that different modes of interactions may occur depending on the amount of water in a given moistened sample. Water may have bulk properties or may be loosely bound or tightly bound, which are called freezing-bound water and non-freezing-bound water, respectively. The latter bound water is not desorbed even if drying takes place under vacuum drying at moderate temperature. At low moisture contents, these bound water molecules may associate with the polar OH groups of cellulose chains or form crosslink between chains. Both of these types of interactions may contribute to the measured dielectric loss. On the other hand, when the number of sites available for these tightly bound water are consumed, additional molecules of water are bound loosely in such a manner so as these water molecules do not further enhance the dielectric loss mechanism. Accordingly, water may act as plasticizer or antiplasticizer depending on its amount and the mode of the interaction of water molecules with the polymer chains.

Plasticizers also were found to have major effects on the secondary relaxation spectra of cellulose esters.<sup>23</sup> The changes recorded are the elimination of the original secondary relaxation and the appearance of a new relaxation process.

Based on the foregoing, the small difference in the absorption loss observed between moistened and dry hydrocellulose residues throughout the whole temperature and frequency ranges studied is to be expected because of the slight amount of adsorbed water retained by the former sample. Therefore, the presence of the very small amount of water in the moistened sample has little effect not only on its dielectric polarization as shown above but also on the observed dielectric loss factor. The absence of an effective amount of adsorbed water in this residue is confirmed by the



results of dispersion loss observed above room temperature at low frequencies, as shown in Figure 8. These results reveal that with such sample no dispersion loss is recorded above room temperature, whereas with moistened hydroxypropyl cellulose and dextran samples, a dispersion loss is recorded. These results agree well with those previously reported.<sup>25,59</sup> In these articles it has been reported that above room temperature a broad dispersion region due to water loss is recorded and that this effect is observed whenever hydrated polysaccharides are investigated in the temperature range where water mobilization and evaporation takes place. The lower the amount of water absorbed by polysaccharides, the higher the temperature water loss occurs. Hence, these results may be taken as good evidence and confirm the above conclusion that most of the sorbed water in the case of moistened hydrocellulose sample evaporates during the different stages of its thermal treatment and that, after heating the sample at 110°C, the resulting sample could be considered as a truly dry sample. Furthermore, before drying the sample at this temperature, the presence of a slight amount of adsorbed water molecules that are still retained by the sample could not be detected by loss measurements above room temperature. It seems likely that this residual water in this case is most probably acting as an antiplasticizer because of the formation of more and strong hydrogen bonds between these water molecules and cellulose chains compared with those in the dry sample. Previous results of infrared spectroscopy<sup>56–58</sup> reveal that more hydrogen bonds have been suggested to be present in samples of very low water contents compared with dry ones. The formation of more and strong hydrogen bonds in this case may suppress the mobility of the polymer units responsible for the dielectric relaxation observed. Accordingly, one could explain the slight shift of the maximum temperature of the absorption loss to slightly higher temperature in the case of moistened hydrocellulose sample compared with the corresponding dry specimen, as shown in Figure 4. Based on these results, one may conclude that the residual water molecules in the case of moistened hydrocellulose residue are not directly involved in the observed relaxation, as will be seen in the case of the absorption loss results found with the other two moistened examined samples. This relaxation peak found below room temperature with dry hydrocellulose sample will be denoted as  $\gamma$ -process. That only one absorption peak is observed in the case of dry polysaccharides, in the temperature and frequency ranges studied, is also observed with hydroxypropyl and dextran dry samples at higher frequencies, as shown in Figure 7(C). The presence of even a small amount of adsorbed water modifies the relaxation spectrum and introduces a new relaxation below room temperature, which is of a different nature compared with that

observed in the truly dry samples, as supported by the activation energy results given in Table I. This relaxation will be denoted here as  $\beta$ -process. In previous works,<sup>20,21,25,37</sup> two relaxations were also recorded: one with dry polysaccharides and the second with hydrated samples. However, although the same  $\gamma$ - and  $\beta$ -notations used here were used before by Montes et al.,<sup>20,21</sup> Einfeldt et al.<sup>39</sup> named the first one as  $\beta$ -process and the second as  $\beta_{\text{wet}}$ -relaxation.

According to the above findings, it appears that, with the different samples studied here, more than one apparent relaxation process could be detected below room temperature. Although almost similar results have been reported by some of the previous authors,<sup>8–41</sup> they do not agree on the origin of the observed relaxations. In this respect, the following is an attempt to analyze and interpret our results to shed more light on the origin of these relaxations and to clarify the contradictions reported by the previous workers.

### $\beta$ -Relaxation process

The most striking features of the above results is the close loss results obtained with both dry and moistened hydrocellulose residue. In addition, the activation energy of the observed loss process is almost the same and a similar value is found for the dry hydroxypropyl cellulose specimen. On the contrary, moistened hydroxypropyl cellulose and dextran samples of 6.0 and 13.0% moisture contents, respectively, show different loss and activation energy results. Furthermore, the dispersion loss observed with these moistened samples above room temperature disappears after drying the samples. Below room temperature, the sizable loss peak recorded with these moistened samples is reduced and shifted to higher temperature with the corresponding dry samples and a second weak loss peak is recorded at lower temperature. These results agree well with those reported before,<sup>8,12,14,17,22,24,25,37</sup> which show that, below room temperature, a broad peak loss was recorded with hydrated polysaccharides. Much discussion has been centered around the contribution of water to this relaxation. Some workers have concluded that the overall process is a combination of motion of methylol groups and methylol–water complexes. However, it has been suggested<sup>8,12</sup> that the free methylol groups take place at lower temperature (–90 to –120°C), whereas that of methylol–water complexes occurs at higher temperature (–50 to –30°C). Recently, Einfeldt et al.<sup>37</sup> summarized and discussed the different relaxation processes found for cellulose and other polysaccharides by investigators studying these materials in the time and frequency range of >0.1 ms and <10 MHz, respectively. The outcome of this work showed that in the dielectric spectra of these materials five

qualitative different relaxation processes were recorded. In this article, it was reported that, below room temperature, cellulosic samples having moisture contents of <15% w/w show a relaxation called by these authors  $\beta_{\text{wet}}$ -process (called here  $\beta$ -relaxation). These authors found that the activation energy of this process varies between 65 and 90 kJ/mol and stated that this relaxation corresponds to a motion of water-polymer complexes and not to individual bound water molecules. Cellulose chains are partially linked by water molecules to a gellike network, and a particular state of motion of this system is measured as the  $\beta_{\text{wet}}$ -process. This interpretation is plausible, but definite evidence for this model and a definition of specific type of molecular motion is so far absent.

The present results agree well with the above findings, which clearly indicate that the presence of even a small amount of water plays an important role in the dielectric relaxation observed. The results also show that a significant change in the loss observed after drying the moistened samples, which is greater in the case of dextran than that of hydroxypropyl cellulose, which could be taken as evidence that the incorporated water in these samples does not act only as a plasticizer but is responsible and directly involved in the molecular motion responsible for the observed  $\beta$ -absorption loss process. This is supported by the results of the activation energy given in Table I, which shows that the activation energy values of the  $\beta$ -process of moistened samples are greater than the values of the  $\gamma$ -process of the corresponding dry samples. Also, higher values for the activation energy of the relaxation process of moistened samples than that observed with dry ones have been reported.<sup>25,37</sup>

In view of the above findings, one may conclude that the kinetic units responsible for the  $\beta$ -relaxation must be complex and could be mainly due to a cooperative motion related to the presence of strongly adsorbed water molecules. This water-induced relaxation could be a result of the formation of a cellulose-water complex occurring in the disordered regions of hydroxypropyl cellulose and dextran. The absence of such an absorption loss in the case of hydrocellulose residue may be due to the different nature of the disordered regions in this rigid material. Furthermore, the increase of the maximum temperature of the  $\beta$ -loss peak in the case of hydroxypropyl cellulose than dextran implies that the difference in the chemical structure of these two materials could be responsible for the hindering effect observed, which is higher in the case of hydroxypropyl cellulose than dextran. This could be accounted for if we assume that the interaction in the polymer-water complex takes place between water molecules and the polar hydroxyl groups of cellulose chains forming a strong association. If so, one has to expect that the water complex formed with the hydroxypropyl side group is of a higher volume than

that formed with the secondary hydroxyl group in the case of dextran and would result in more restriction of the molecular motion of the observed  $\beta$ -loss process. In accordance with this interpretation is the higher activation energy value obtained in the case of hydroxypropyl cellulose compared with that of dextran. In addition, the shift of this loss peak to higher temperature on drying and its appearance only with the highly disordered hydroxypropyl cellulose and dextran and not with the highly crystalline hydrocellulose sample reveal that this process takes place when interactions occur between OH groups in the highly disordered regions of the polymer, if present, and water molecules.

### $\gamma$ -Relaxation process

It is evident from Figures 5 and 6 that, after evaporation of water, the resulting dry hydroxypropyl cellulose and dextran samples at relatively low frequencies show two weak loss peaks in which the intensity of the  $\beta$ -loss peak observed with the corresponding moistened samples is reduced and shifted to higher temperature and a second loss appears at lower temperature, agreeing well with a previous investigation.<sup>25</sup> This implies that the presence of the strong cellulose-water complex in the latter specimens, which results in the appearance of the sizable  $\beta$ -process, is capable of inhibiting the original low temperature and the relatively weak  $\gamma$ -relaxation observed in the dry polymers. The results as shown in Figures 5(B) and 6(B) also show that the weak absorption peak observed at high temperature in the dry hydroxypropyl cellulose and dextran samples gradually disappear with increasing frequency. At the same time, the intensity of the low-temperature absorption peak increases and shifts to higher temperature. The results given in Figure 7(C) indicate that, in the temperature range ( $-50$  to  $0^\circ\text{C}$ ) at frequency ( $5.9 \times 10^2$  kHz), only one relaxation is observed with all samples examined irrespective of their chemical or fine structure. The results also show that the height of the recorded absorption peaks decreases in the following order: hydrocellulose > hydroxypropyl cellulose > dextran, while the reverse takes place regarding the change in broadening of the observed peaks. That only one apparent absorption peak exists with the dry samples agrees well with the results of hydrocellulose sample, which shows that, in the absence of the highly disordered structure in this residue and in turn the lack of incorporated water in its inner fine structure, only one apparent loss peak is recorded with both the slightly moistened and the dry samples as stated above.

Regarding the molecular origin of this relaxation peak, Einfeldt et al.,<sup>37</sup> after reviewing the literature in this field, stated that the process under discussion could not be explained by a methylol side group mo-

tion in the case of unsubstituted polysaccharides as some of the previous authors claimed<sup>20,21</sup> but as segmental motion of the chain and side group motion as additional process. Furthermore, the authors<sup>37</sup> added that, in the case of cellulose derivatives, the reorientation of bulky side groups needs a simultaneous motion of the main chain for spatial reasons. Consequently, the position and distribution on the frequency scale of the suggested relaxation found in cellulose derivatives are indirectly determined by the  $\beta$ -relaxation under discussion (the  $\gamma$ -relaxation here).

In view of these findings, the observed relaxation process is quite complex and the assignment of the relaxation process to a specific molecular motion is not easy. However, a comparison between the results obtained by the highly crystalline hydrocellulose possessing methylol side group and the highly disordered dextran sample without methylol side group led one to suggest that, in unsubstituted polysaccharides, the observed  $\gamma$ -relaxation process of activation energy of 39.9 kJ/mol in the case of the former sample, which is greater than that of dextran amounting to 32.0 kJ/mol, could be assigned to local segmental motion of some glucose units and that this motion depends on the nature of the glucosidic linkage and that the conformational freedom about  $\alpha(1-6)$  linkage is higher than the  $\beta(1-4)$  linkage. In addition, the appearance of this process at almost at the same temperature and frequency for both samples that contains methylol or hydroxypropyl groups and with the same activation energy amounting to almost 40 kJ/mol could be accounted for either to a localized segmental motion of the main chain or to more than one molecular process superimposed in the empirical peak. To shed more light on this problem, a detailed investigation is currently being carried out in this laboratory on the dielectric behavior of some cellulose derivatives.

The results as shown in Figures 4–7 reveal that the change in shape, intensity, and size of the peak under discussion from one sample to the other shows that the distribution of both the inter- as well as the intramolecular interactions that contribute to this relaxation process is different and is lowest in the case of hydrocellulose, intermediate with hydroxypropyl cellulose, and highest in the case of dextran. In accordance with this is the results and analysis given above concerning the changes of the dielectric constant that takes place during drying. These results show that viscose hydrocellulose sample is of highly crystalline structure and of strongly hydrogen disordered regions compared with the relatively weak hydrogen-bonded regions in disordered structure of the two other test samples, which is higher in the case of dextran than the corresponding regions in hydroxypropyl cellulose. Accordingly, less distribution of intermolecular forces is expected to predominate in the case of the dry hydrocellulose sample and thus more unification of

the observed relaxation occurs compared with the higher distribution in the case of the two other samples, which is highest in the case of dextran. Therefore, the characteristic features of the observed  $\gamma$ -relaxation in dry samples are dependent on several factors, namely, the glucosidic linkage, the fine structure of the polysaccharide, and the size as well as the polarity of the substituent group of glucose unit. Besides, this relaxation process is very sensitive to both water of hydration and the frequency used in dielectric measurements.

It seems worthy to pay attention to the discrepancies reported by various authors<sup>8–41</sup> concerning relaxation phenomena in the hydrophilic materials that could be mainly due to the difficulty in obtaining truly dry samples. The problem arises when comparing the viscoelastic spectra of these materials in the impossibility of referring to identical levels of hydration. The so-called dry samples used in some of the previous investigations most probably contain some residual water, the amount of which depends on the chemical and the fine structure of the examined sample and the experimental method used for drying. According to these views together with the sensitivity to water of hydration of all relaxation processes reported with polysaccharides, the original molecular dynamic loss in these materials may be hidden behind, suppressed, or even disappeared from one study to the other depending on the drying condition employed. This is what is confirmed in the present work in which the  $\gamma$ -peak has been observed with hydrocellulose residue, which is considered to be an almost completely dry sample, while, with the moistened hydroxypropyl cellulose and dextran samples, this peak is hidden behind the sizable water-induced  $\beta$ -peak, and, even after vigorous drying, two weak loss peaks are recorded. The  $\gamma$ -loss peak appears well without the interference of the loss because of the presence of polymer–water relaxing units, only at higher frequencies.

Finally, the analysis of the dielectric results obtained here and the satisfactory interpretation given clarify to a great extent the contradictions reported in the literature concerning the relaxation phenomena in the complex polysaccharide–water system.

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