Dielectric studies of proton migration and relaxation in wet cellulose and its derivatives

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Dielectric relaxation data are reported over a frequency range 400 Hz to 12 kHz and over a temperature range 193 to 323K on cellulose, cellulose acetate and ethyl cellulose with various water contents. A relaxation peak shifted to the low temperature side of the beta process was observed for cellulose acetate with less than 4% water. The effect of water addition in the case of cellulose and ethyl cellulose was initially to increase the amplitude of the loss associated with side group motion. Above 4% water content, the low temperature relaxation in cellulose acetate moves to lower temperatures and an increase in the loss is observed at high temperatures. Similar behaviour was observed in cellulose and ethyl cellulose. A transformation of the frequency dependent conductivity data allowed identification of a hopping conduction process at high temperature. The lowest temperature processes are analyzed in terms of dipole relaxation and the higher temperature features in terms of proton migration.

INTRODUCTION

A recent review of the relaxation behaviour in cellulose and its derivatives[1] indicated that there exists some controversy over the effects of water on the dielectric properties. A recent paper[2] has proposed that the observation of a marked increase in the dielectric loss at high temperatures in cellulose containing water is associated with plasticization of the alpha relaxation peak. An alternative hypothesis has been put forward based on dielectric and infra-red studies[3–6], attributing the increased loss to the generation of free charge carriers. This paper is concerned with a detailed systematic investigation of the addition of water to cellulose, cellulose acetate and ethyl cellulose. As discussed previously[1] the dielectric relaxation of 'dry' cellulose and its derivatives consists of at least two relaxation features[7–9]; a high temperature feature associated with the onset of interchain motion and associated with the break up of the ordered internal states of fibril structures and a lower temperature feature associated with the reorientation of dipoles in the surface of the fibrils or in amorphous regions. The latter relaxation occurs at approximately 273K in cellulose acetate and at around 213K in cellulose and ethyl cellulose. The higher temperature feature lies around 373K and above in most cellulose derivatives. The stability of the internal fibril structure has been demonstrated by deuterium infra-red studies which indicate that only a small proportion of the available hydroxyl groups can be readily exchanged at room temperature[3–6]. It has been further shown that substitution of hydroxyl groups leads to shifts in the OH stretching vibration from 3400 cm^{-1} to a new position which is sensitive to the nature of the substituent[4]. When a hydrogen bond is formed between a hydroxyl group and a neighbouring hydrogen atom, the bond length of the OH increases and the force constant decreases. Hence substitution has the effect of weakening the degree of hydrogen bonding with a result that the OH stretching vibration is shifted to higher frequency. The net result of the substitution is therefore to firstly substitute accessible surface hydroxyl groups and then to introduce disordered regions by reacting with the internal hydrogen bonded states. If substitution of hydroxyl groups is incomplete, as in the materials studied here, structure will be retained. The temperatures used in this study are well below those at which structural rearrangement is possible.

The observation of a rapidly increasing conductivity with increasing frequency is typical of that observed for charge carrier migration in amorphous materials[10]. The addition of water may be anticipated to have both the effect of plasticization of the polymer and also can provide a source of charge carriers (protons). Both effects may be considered to influence the dielectric properties of the material and this paper is concerned with the presentation of new data on the effects of water and analysis of this information in terms of various possible models.

EXPERIMENTAL

Materials and sample preparation

All the samples used in this study were supplied by Dr T. Lewis, PERME (WA), their substitution characteristics are summarized in *Table 1.*

The materials used were dried in an oven at 363K for 24 h before use. In this study discs of 5 cm diameter were

Table 1 Substitution characteristics of cellulose derivatives

Polymer	Substitution γ_{OH}	 γ_{CH_3COO}	 $\gamma_{OCH_2CH_3}$
Cellulose	300	–	–
Cellulose acetate	46	254	–
Ethyl cellulose	42	–	258

γ_x – indicates the amount of substitution per hundred glucopyranose rings. Ash content for cellulose acetate = 0.2%

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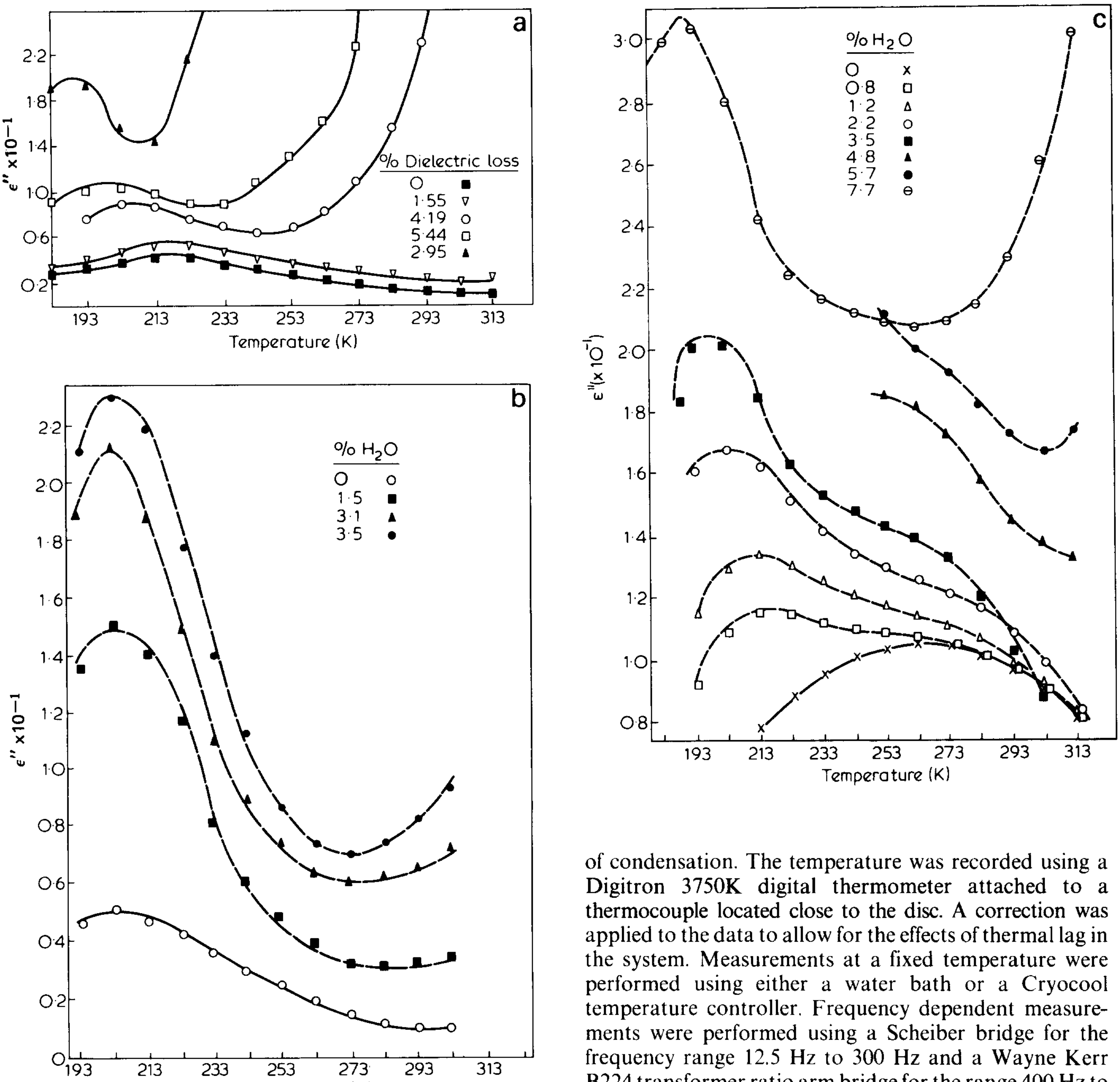

Figure 1 (a) Variation of the dielectric loss at 1 kHz *versus* temperature for cellulose. (b) ethyl cellulose and (c) cellulose acetate with various water contents

prepared by pressing the materials at 373K and a pressure of 38.4 MPa. Various degrees of hydration were achieved by placing the discs for different lengths of time in a desiccator containing distilled water. The degree of water uptake was estimated by weighing the sample before and after the experiment; the difference between these values was typically less than 0.26%. The permeation of water into these samples has been discussed previously[1].

Dielectric measurements.

The dielectric data were recorded as a function of temperature at a fixed frequency of 1 kHz using a Teradyne C357 automatic bridge and a two terminal cell configuration. The cell was flushed with dry nitrogen prior to cooling the sample and contained a drying agent (using silica gel) as an added precaution against the effects of condensation. The temperature was recorded using a Digitron 3750K digital thermometer attached to a thermocouple located close to the disc. A correction was applied to the data to allow for the effects of thermal lag in the system. Measurements at a fixed temperature were performed using either a water bath or a Cryocool temperature controller. Frequency dependent measurements were performed using a Scheiber bridge for the frequency range 12.5 Hz to 300 Hz and a Wayne Kerr B224 transformer ratio arm bridge for the range 400 Hz to 12 kHz. The d.c. conductivity was measured as a function of water content using a Keithley 610C electrometer. Comparison of uncoated and coated with graphite indicated that there are negligible contributions from electrode polarization to the observed dielectric properties.

RESULTS AND DISCUSSION

Temperature-water content studies

The effect of temperature and water content on the dielectric loss at 1 kHz was investigated for cellulose, *Figure 1a*, cellulose acetate, *Figure 1b*, and ethyl cellulose, *Figure 1c*. The positions of peaks in the loss observed for the dry samples are in agreement with those reported by other workers[7–9]. The effect of addition of small amounts of water to cellulose leads to an increase in the hydroxyl side group motion. Further addition leads to the peak in the loss moving to lower temperatures and also the observation of a marked increase in the dielectric loss at high temperatures. A similar variation was observed in

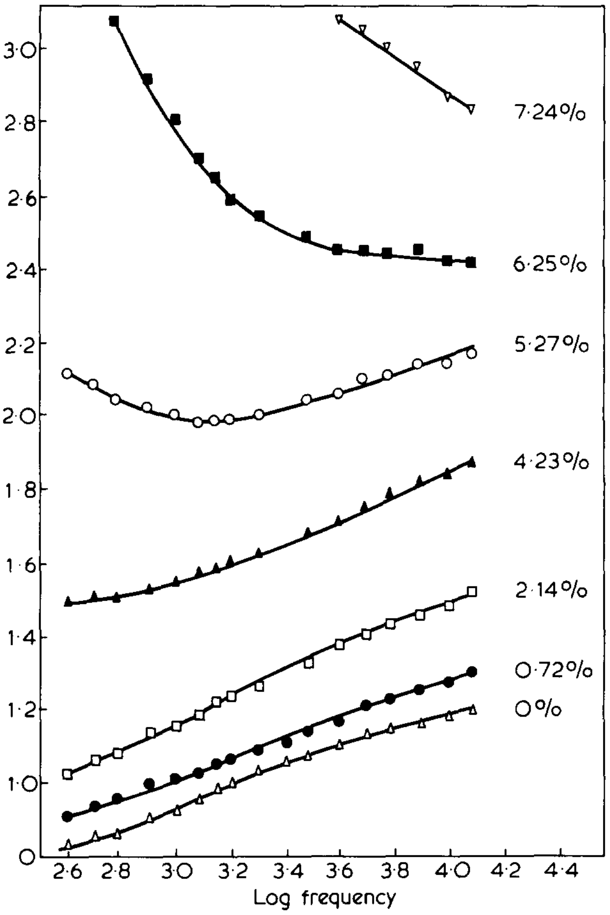

Figure 2 Variation of dielectric loss *versus* frequency for wet cellulose acetate with various water contents at 295K

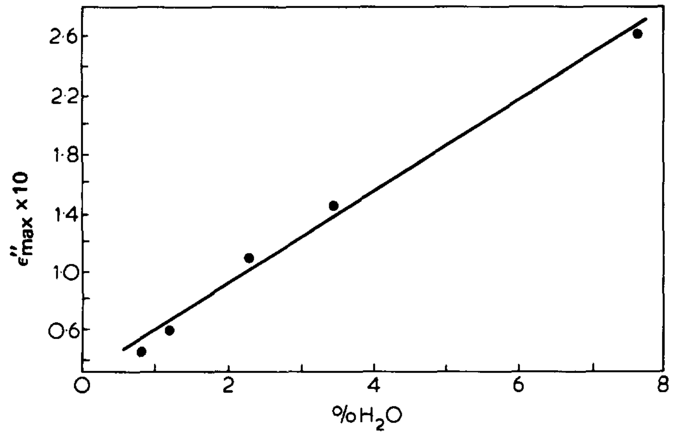

Figure 3 Amplitude of the resolved low temperature water peak *versus* water content. ε'' 'wet'−ε'' 'dry' for cellulose acetate at 1 KHz

ethyl cellulose, *Figure 1b*. In contrast, the relaxation of the side chain of the cellulose acetate and the water molecules are resolved. As in the previous cases, increasing the amount of water present above some critical value leads to the appearance of an increase in the high temperature dielectric loss. The loss features in the dry samples can be attributed to the reorientation of hydroxyl, ether and acetate groupings in cellulose, ethyl cellulose and cellulose acetate, respectively. In an attempt to define more precisely the effect of change in water content on the dielectric properties the permittivity and loss were investigated as a function of frequency. At high temperatures, ~295K plots similar to those observed for cellulose acetate were observed, *Figure 2*. An increase in the dielectric loss towards high frequency is typical of the occurrence of a relaxation process at low temperature at 1 kHz. Similarly, the observation of an increase in the loss towards low frequency is indicative of a relaxation at high temperature at 1 kHz. This low frequency feature may be attributed either to a shift in the alpha relaxation with the addition of water or to the presence of charge carrier migration. The analysis of the data can be separated into two sections: investigation of the temperature dependence of the low temperature peak and analysis of the high temperature properties.

Analysis of the reorientation motion of water

Subtraction of the loss due to the side group motion defined in the study of the dry sample from the observed loss in the wet samples yields a peak, the amplitude of which varies approximately linearly with the concentration of water molecules, *Figure 3*. Transfer to the frequency domain indicates that the relaxation due to the added water occurs at lower temperatures–higher frequencies than the side group motions. The dielectric relaxation associated with this process was observed to spread over several decades (*Figure 4*) and analysis of the data was achieved using the Cole–Cole method of analysis (Appendix I). The relaxation frequencies obtained from this analysis were then used to construct activation energy plots of the type shown in *Figure 5*. It is apparent that the

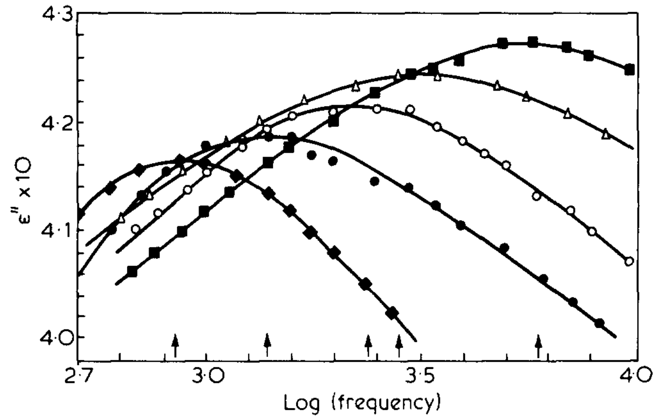

Figure 4 Temperature dependence of the dielectric loss for cellulose acetate with 4.79% water

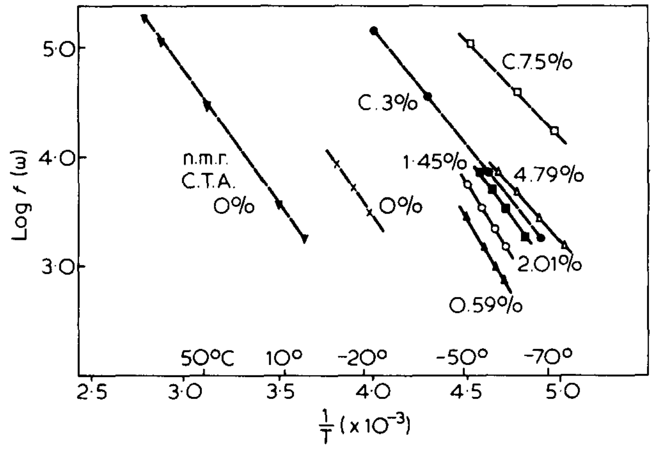

Figure 5 Activation energy plot for cellulose and cellulose acetate with various water contents. Water content x, 0%; ▲, 0.59%; ○, 1.45%; ■, 2.01%; ●, 3%; △, 4.79%; □, 7.5% H_2O

Table 2 Relaxation parameters for cellulose acetate

Percentage water %	Activation energy ΔH^{+} kJ mol^{-1}	Pre-exponential factor $-A$ s^{-1}	Entropy ΔS^{+} JK mol^{-1}	Distribution parameter β
0	46.78	1.48×10^{13}	7.98	0.14
0.59	56.44	4.75×10^{16}	17.6	0.15
1.45	56.65	1.06×10^{17}	81.8	0.16
2.01	43.68	1.46×10^{14}	27.04	0.14
4.40	30.08	1.65×10^{11}	−29.41	0.13
4.79	30.71	1.79×10^{11}	−28.76	0.10

water relaxation is well resolved from that of the side group motion in cellulose acetate and this allows activation energies for the reorientational motion to be derived using the rate equation:

$$\tau = \frac{h}{kT}\exp\left[\frac{\Delta H^{+}}{RT}\right]\exp\left[\frac{-\Delta S^{+}}{R}\right] \tag{1}$$

where ΔH^{+} and ΔS^{+} are respectively the enthalpy and entropy of activation for the reorientational motion of the hydroxyl group and the remaining symbols have their usual meanings, $\tau = (2\pi f)^{-1}$. The parameters obtained from the analysis of this data are summarized in *Table 2*.

The temperature range used in this analysis is rather restricted and therefore the pre-exponential factor and the entropy are subject to a high degree of uncertainty. However, the changes in the activation energy are greater than the experimental error which is typically ±5 kJ mol^{-1}. The activation energy for the reorientational motion of the acetate group has a value of 46 kJ mol^{-1}, comparable with that reported by other workers[11,12]. The values for the wet systems are for the reorientational process of the water molecules. The activation energy appears to decrease with increasing water content, *Table 2*. Estimates of the surface area based on *BET* measurements and using nitrogen as the absorbant gas indicate that the available surface area is approximately 150 m^2/g [13]. Assuming the area of adsorbed water is 14 Å [14]; monolayer absorption would be expected to occur at approximately 4.5%. The dielectric relaxation at low water contents may therefore be adsorbed to 'molecularly' dispersed water and the dipole reorientation is probably closely associated with the motion of the acetate side group to which it is bound. Increasing the water content will tend towards a monolayer formation and a loss of specificity of the nature of the binding site.

Studies of water adsorbed on silica have indicated that if the molecules exist in less than a bilayer, the associated dielectric loss is observed to occur at low temperatures[15], ~190K. Once multilayer absorption has occurred an additional feature is observed at approximately 273K similar to that observed in ice[16]. The temperature dependence of the dielectric relaxation yields an activation energy for water adsorbed on alumina of 50 kJ mol^{-1} at low temperatures and a value of 26 kJ mol^{-1} at high temperatures[17]. The reason for this change in activation energy is not clear but appears to be associated with the occurrence of facile hopping processes.

Water in a mono-bilayer situation will reorientate by breaking and reforming of two hydrogen bonds. A hydrogen bond will be anticipated to have a dissociation energy of approximately 14 kJ mol^{-1} which would lead to a prediction of about 28 kJ mol^{-1} for the relaxation once a 'water-like' situation has been developed. The observed trends are in good agreement with these predictions.

Higher temperature increases in the dielectric loss have been ascribed to plasticizations of the main backbond motion[2,3]. Mechanical relaxation studies of cellulose acetate with various degrees of hydration up to 5% water content have indicated that there is no appreciable change in the high temperature alpha process[11,12], however changes in the low temperature profile have been observed. The alternative hypothesis that the observed increase in the dielectric loss is associated with charge carrier-proton migration is favoured in this study.

Charge carrier-proton migration

It has been observed that despite large differences in composition and structure, charge conduction in amorphous solids can be described by a simple law of the form[18]

$$\sigma(\omega) = A(T)\omega^{n(T)} \tag{2}$$

where $A(T)$ and $n(T)$ are weakly temperature dependent parameters and n has a value in the range 1.1–0.5 and frequently is just less than unity (*Figure 6*). At sufficiently low frequencies, departure from the law represented by equation (2) may be expected and is often found experimentally; $\sigma(\omega)$ is found to tend towards either an ω^0 or ω^2 behaviour. In practice, $\sigma(\omega)$ should be added to the true d.c. conductivity σ_0 which is strictly speaking not the limit of $\sigma(\omega)$ as ω tends to zero, but represents a different mode of conduction in which charge carriers are physically

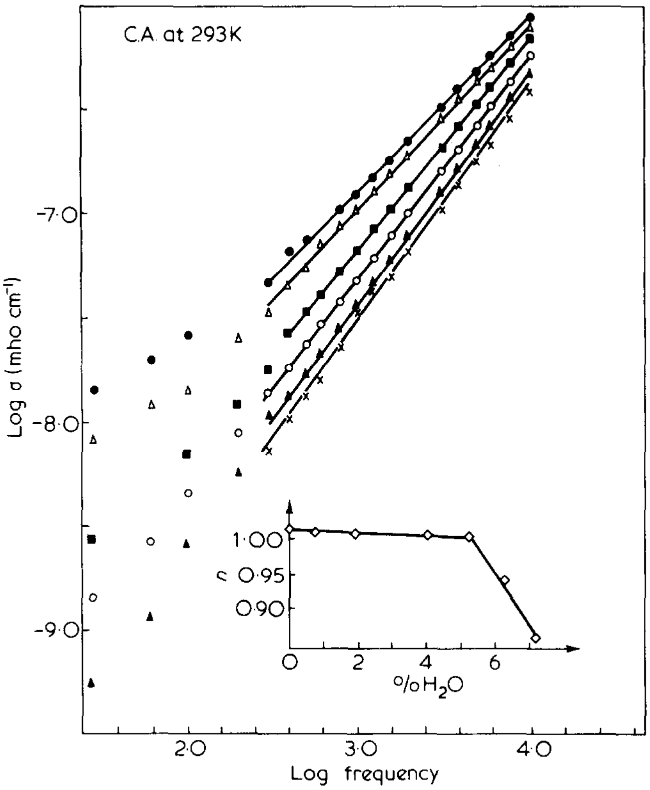

Figure 6 Variation of the a.c. conductivity with frequency as a function of water contents, $\sigma(\omega) = \omega^n$, for cellulose acetate 293K. Inset is the variation of the coefficient n-equation[2] with water content. Water content ×, 0%; ▲, 2.2%; ○, 4.2%; ■, 5.3%; △, 6.3%; ●, 7.3%

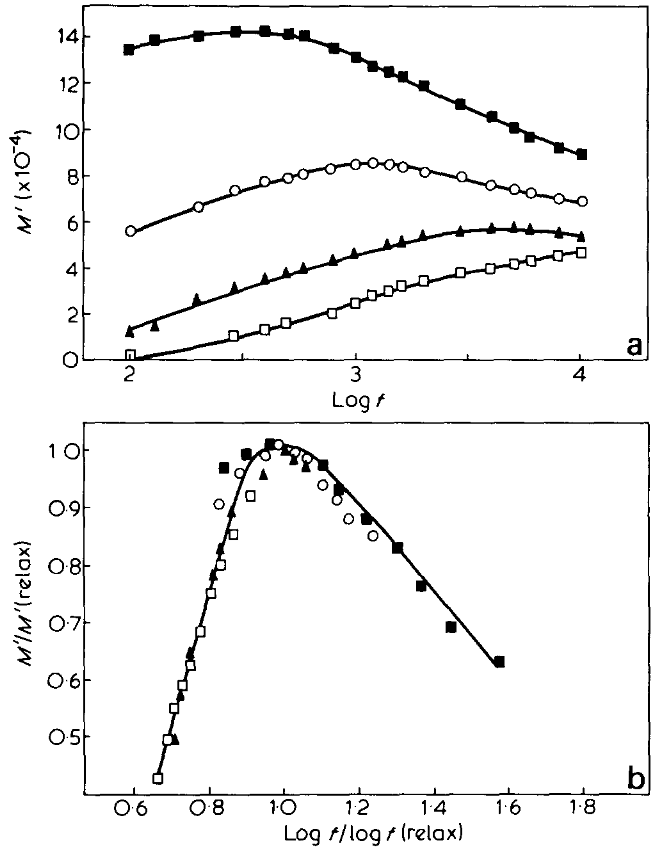

Figure 7 (a) Variation of M' with frequency for various water contents and (b) the normalized water curve for cellulose acetate. Water content ■, 4.23%; ○, 5.27%; △, 6.25%; □, 7.24% H_2O

transported right through the solid as the result of the application of a steady field.

It has been pointed out by Bakr *et al.*[19] that the modulus representation provides a convenient method of separating the various contributions to the complex permittivity when conduction processes are present:

$$\varepsilon(\omega)^* = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon'(\omega) - i[\sigma(\omega)/\omega e_0] \tag{3}$$

where ε^*, ε' and ε'' are respectively the complex, real and imaginary permittivities; $\sigma(\omega)$ is the total conductivity measured at frequency ω and e_0 is the permittivity of free space (8.854×10^{-12} F m^{-1}). For materials of low conductivity the imaginary part can be separated into a linear sum of relaxation and conduction components:

$$\varepsilon(\omega)^* = \varepsilon'(\omega) - i(\varepsilon''_{\text{relax}} + \sigma_0/\omega e_0) \tag{4}$$

For highly conducting materials it is convenient to adopt the electrical modulus form[21,22] as an analysis of a conductivity relaxation is required:

$$M^*(\omega) = 1/\varepsilon^*(\omega) = M'(\omega) + iM''(\omega) \tag{5}$$

where

$$M'(\omega) = \frac{\varepsilon'(\omega)}{[\varepsilon'(\omega)]^2 + [\sigma(\omega)/\omega e_0]^2} \tag{6}$$

and

$$M''(\omega) = \frac{\sigma(\omega)/\omega e_0}{[\varepsilon'(\omega)]^2 + [\sigma(\omega)/\omega e_0]^2} \tag{7}$$

The ideal (Maxwell) RC circuit, defined as the situation where the real permittivity is independent of frequency ε_s, leads to a relaxation time of the form

$$\tau_M = \varepsilon_s e_0/\sigma_0 \tag{8}$$

where τ_M is the Maxwell relaxation time and ε_s the static permittivity. Using equation (8) the ideal complex modulus $M_M^*(\omega)$ has the form

$$M_M^*(\omega) + M_\infty \frac{i\omega\tau_M}{1 + i\omega\tau_M} = M_\infty \frac{(\omega\tau_M)^2 + i\omega\tau_M}{1 + (\omega\tau_M)^2} \tag{9}$$

where $M_\infty = 1/\varepsilon_\infty$ is the electrical modulus at frequencies much higher than those of the relaxation region.

Figure 6 clearly indicates the correctness of equation (2) in describing the conduction behaviour in the hydrated cellulose systems. Using equations (6), (7) and (8) the data on cellulose acetate were transformed into the modulus representation (*Figures 7* and *8*). The data obtained at various water contents may be shifted onto a common master curve for M', (*Figure 7*) and M'' (*Figure 8*). The master curve, *Figure 8*, approximates to that of an ideal process with a maximum at 293K at 5 kHz for a water content of 6.25%. This observation implies a mean hopping time of 3.18×10^{-5} s, predictions based on hopping theory[22] yield a value of 8.28×10^{-5}.

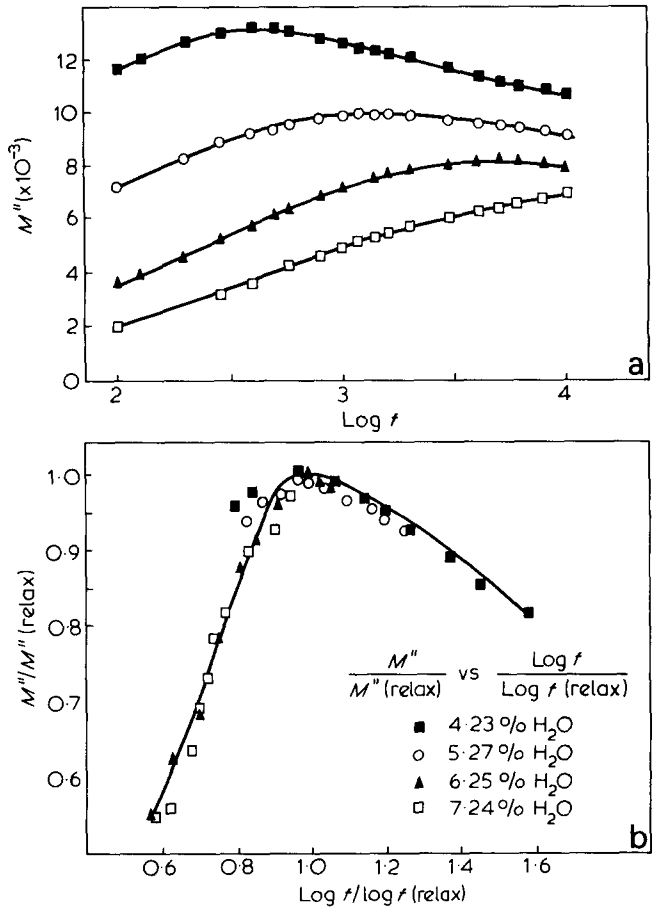

Figure 8 (a) Variation of M'' with frequency for various water contents and (b) the normalized master curve for cellulose acetate. Key as for *Figure 7*

The problem of charge carrier hopping between localized sites in amorphous solids has been considered theoretically by Mott[22], Pike[23] and Lewis[24]. It has been pointed out that if energy states exist in the band gap then the coefficient n in equation (2) will not remain constant but will fall below unity and $\sigma(\omega)$ will become independent of ω. This is typical of the behaviour observed in this study. At low water contents the hopping process presumably occurs between well defined bound sites and n has a value of just above unity; formation of a multilayer situation and the commensurate loss of specificity of the binding site leads to a decrease in the value of n to below unity and the observation of a change in the frequency dependence of the a.c. conductivity. The mechanism of conduction may be pictured in terms of rotation of a hydroxyl group followed by dissociation and subsequent proton migration. It is easy to visualize that in the monolayer situation various states may appear within the energy gap[25,26]. Similar situations have been identified in polypeptide structures; the energy gap in this case being approximately 3.2 eV with widths of approximately 1 eV [27,29]. The proton conduction may be anticipated to be similar to the random energy activated hopping described by Pike[23]. If it is assumed that the sites are singly occupied and that the probability of activation is $\frac{1}{4}$ then the a.c. conductivity has the form

$$\sigma(\omega) \propto N^2 \omega^{1-\beta} \tag{10}$$

where $\beta = 6kT/W$, where W is the energy difference between the bound site and the conduction band. Using equation (10) with the data in *Figure 6* yields a value of W equal to 2.43 eV at 6.3% and decreases to 0.97 eV at 7.3%. These values are considerably lower than those observed in the polypeptides, however in the cellulose systems, proton conduction involves water molecules rather than dissociation of a peptide linkage and may be expected to be a more facile process. The observed approximately exponential increase in the a.c. conductivity, *Figure 1*, with increasing temperature is also consistent with the predictions of this model.

CONCLUSIONS

The dielectric relaxation of cellulose and its derivatives when hydrated can be described in terms of two well defined regions; a low water content regime where water molecules are associated with specific sites and their reorientation motion couples with that of the side group to which they are attached. At higher water contents, mono and bilayer structures are formed with a commensurate change in the mobility of the protons, loss of specificity of the binding site and shift of the low temperature relaxation process to higher frequencies than those observed for side chain motion.

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APPENDIX I

The relaxation of a water molecule may be approximated to that of a Cole–Cole depressed semi-circle which is obtained from the equations of Havriliak and Negami[30] by placing $\alpha = 0$. In which case the dielectric loss has the form

$$\varepsilon''(\omega) + r^{-\beta/2}(\varepsilon_0 - \varepsilon_\infty)\sin(\theta\beta) \tag{A1}$$

where

$$\theta = \frac{\arctan(\omega\tau_0)^{(1-\alpha)}\cos\alpha\frac{\pi}{2}}{1+(\omega\tau_0)^{(1-\alpha)}\sin\alpha\frac{\pi}{2}} \tag{A2}$$

At the maximum $\varepsilon''_{\max}$, $\omega\tau_0 = 1$ in which case (A2) reduced to $\theta = 45°$. Equation (A1) can then be rearranged into

$$\frac{\varepsilon''(\omega)}{(\varepsilon_0 = \varepsilon_\infty)} = r^{-\beta/2}\sin(\theta\beta) \tag{A3}$$

Hence placing $\theta = 45°$ the value of β, *Table 2*, may be obtained by fitting the maximum in $\varepsilon''(\omega)$ to equation (A3).