

Conductivity and Water Sorption in Paper

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Synopsis

Under equilibrium conditions the dependence of the electrical conductivity of cotton cellulose (Whatman 42 ashless filter paper) on moisture content was of an exponential type up to 3.5%. The transient conductivity of paper undergoing water sorption has been measured concurrently with the transient moisture content. The transient conductivity was greater than that at steady state, the difference increasing with decreasing initial moisture content. The results are explained in terms of thermal effects due to the heat evolved during water sorption.

INTRODUCTION

Cellulose has a strong affinity for water and moisture is a determining factor in its electrical conduction. The electrical conductivity of cellulose rises by 12 orders of magnitude as the relative humidity is increased from 1% to 99%.¹ Water may influence both the processes of charge carrier generation and the mechanism of transport. Water affects electrical conductivity directly by its own dissociation, increasing the effective dielectric constant, thus facilitating the dissociation of impurities, and forming, at high water content, layer of high conductivity. Water also affects conductivity indirectly by sorption heat evolved and changes occurring in the cellulose structure.

During water sorption a significant amount of heat is evolved,² particularly in the initial period, causing an increase in the temperature of the sample. The thermal activation energy of conductivity in paper exceeds 1 eV^{3,4} so that even small variations in sample temperature may lead to remarkable changes in electrical conductivity. The temperature increase of the sample due to sorption heat is a time-dependent phenomenon so that the existence of transient electrical currents may be expected.

The kinetics of the water diffusion process is another factor influencing the moisture content-conductivity relationship. During water sorption, there exists a concentration profile throughout the sample, until equilibrium is reached. The time dependence of the electrical conductivity during water sorption should therefore reflect the distribution of water in the sample and be related to the water diffusion process.

Most publications on the dependence of conductivity on water content in cellulose have dealt with steady-state conduction under equilibrium conditions.^{1,5-8} In this work we report on a kinetic study of the water dependence of conductivity as humidity is changed at different rates.

EXPERIMENTAL

Whatman 42 ashless filter paper was used. A schematic diagram of experimental system is shown in Figure 1. It consists of: Cahn electrobalance, RG Type; Keithley Electrometer Model 615; high stability voltage supply,

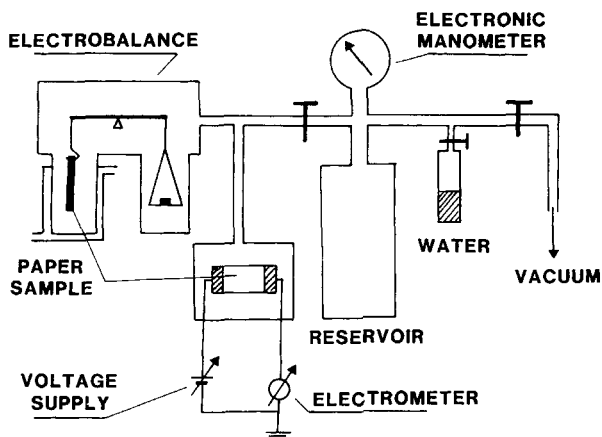


Fig. 1. Experimental setup.

Keithley Model 240A; a vacuum system with electronic manometer (membrane type pressure head gauge MKS Baratron); and a multichannel strip chart recorder. A sample of paper is placed on the electrobalance in the sorption chamber. Another sample is placed in the conductivity cell. Gallium-indium liquid alloy electrodes were used to minimize contact resistance. The electrodes were 11 cm wide and the interelectrode gap was 3mm so that, even with the dry sample, a measurable current could be obtained.

In a typical experiment, the system was degassed overnight at 10^{-3} Torr. Then the desired water vapor pressure was established by means of the vapor reservoir. Weight increase, vapor pressure, and current were recorded simultaneously, as a function of time.

The voltage applied across the sample depended on the water content and was adjusted to ensure a negligibly small polarization current: 200 V at relative humidity up to 30%, 40 V between 30% and 60%, and 5 V above 60% RH.

Electrical conductivity was calculated from

$$\sigma = I/VL/(WT) \quad (1)$$

where I = measured current, V = applied voltage, L = interelectrode gap, W = sample width, and T = sample thickness.

RESULTS AND DISCUSSION

The following types of experiments were performed:

1. Steady-state conductivity (at equilibrium water content).
2. Conductivity response to slow (~ 0.5 Pa/s), quasilinear changes in water vapor pressure (increase or decrease).
3. Conductivity response to a step change in water vapor pressure (step increase or step decrease).

Steady-State Conductivity

Figure 2 shows the steady-state conductivity of Whatman 42 paper against water content plotted on a semilogarithmic scale. For water content between 0% and 3.5% the experimental points, covering a range of conductivity of

five decades, lie along a straight line. This indicates that, in this region, the water dependence of conductivity can be represented by

$$\sigma = \sigma_d \exp(b\alpha) \quad (2)$$

where σ_d = conductivity in the dry state, α = water content, and b = experimental constant.

For the paper investigated, $\sigma_d = 2.15 \cdot 10^{-17} \Omega^{-1} \cdot \text{cm}^{-1}$ and $b = 3.29$. At water content above 3.5% a deviation is observed.

The exponential relationship between steady-state conductivity and water content suggests that there is a single mechanism of conduction in paper for water content between 0 and 3.5 per cent. In this region structural bonding of water to cellulose takes place. The observed relationship is similar to that found for hemoglobin,^{9,10} keratin,¹¹ insulating paper,¹² and some polar polymeric materials.¹³ Excellent survey of the hydration-dependent conductivity in biological materials has been recently given by Pethig.¹⁴

Deviation from linearity observed at water content above 3.5% is probably due to structural changes in the cellulose. It has been reported^{15,16} that the density of cellulose fiber initially increases on addition of water up to around 3–4% before it decreases monotonically with water content due to swelling. This suggests that there is a net contraction in the fiber structure before swelling takes place. Similarly, the refractive index of cellulose fibers shows a maximum around 3.5%.¹⁷ The deviation from linearity likely reflects the swelling in the fiber structure.

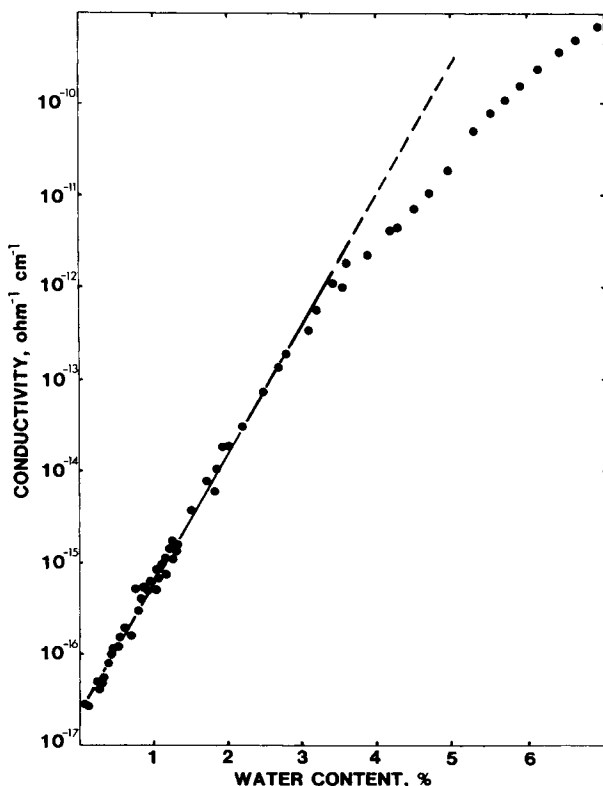


Fig. 2. Conductivity vs. moisture content under steady-state conditions.

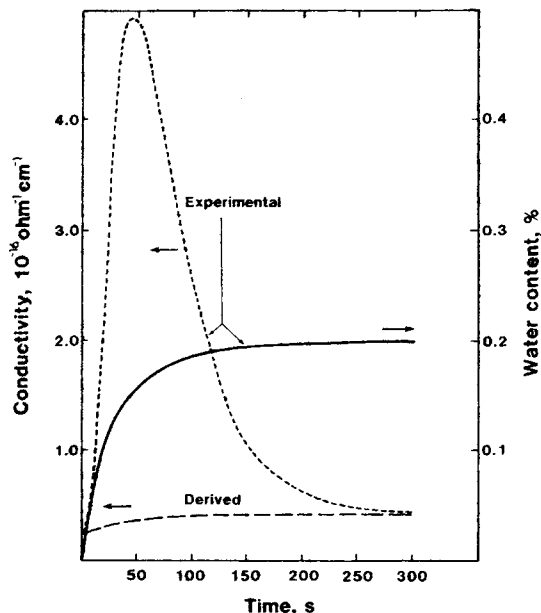


Fig. 3. Actual curves of the change in conductivity with the time when a step change in water vapor pressure is introduced: initial moisture content 0%; vapor pressure change 0–0.15 Torr.

Slow Change in Humidity

The conductivity–moisture content relationship for slow (~ 0.5 Pa/s) changes in vapor pressure was identical to that shown in Figure 2.

Transient Measurements—Step Changes in Humidity

Low Water Content, Small Humidity Steps

Figure 3 is a typical curve obtained at low initial moisture content using a small step change in vapour pressure (0.15 Torr). Three curves are shown: moisture content vs. time (experimental); conductivity vs. time (experimental); conductivity vs. time, “expected” if the variation of current with moisture content were according to Figure 2. This is a derived curve. The experimental curve shows a peak σ_{\max} , which is absent from the “expected” curve. The magnitude of the peak current expressed as $\Delta I = I_{\max} - I_{\infty}$, where I_{∞} is the final steady state value, depends on the initial water content, and is given in Figure 4 for step changes of the order of 0.15 Torr. The magnitude of the peak current is rapidly decreasing with increasing water content, reaching zero at around 1%.

Low Water Content, Large Humidity Steps

Figure 5 is a typical curve for an experiment where a large step change in relative humidity (from 0% to 20% or 30% RH, for example) is applied. No current peak is observed, but deviation from “expected” behavior is still present.

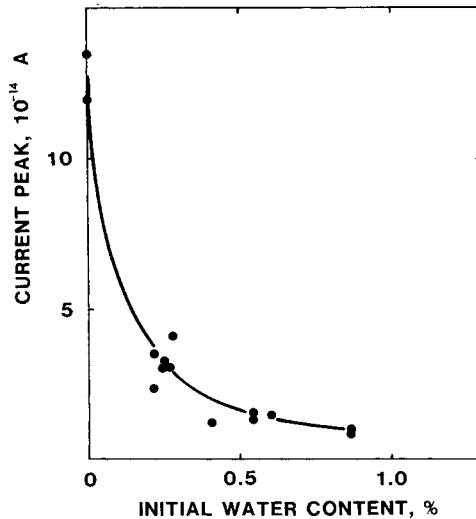


Fig. 4. Dependence of current peak height $\Delta I = I_{\max} - I_{\infty}$ on initial water content for step changes in RH of the order of 1%.

Since both conductivity and moisture content were measured at the same time during these experiments, cross plots of conductivity vs. moisture content can be prepared and compared to that of Figure 2 obtained under steady-state conditions. This has been done in Figure 6. Note that, at a given moisture content, transient conductivity can be much higher than the steady-state value and the deviation increases with increasing step change in pressure (curves 2, 3, and 4, respectively). Figure 7 shows that the effect is also present (though reversed) during a step desorption experiment (curve 3).

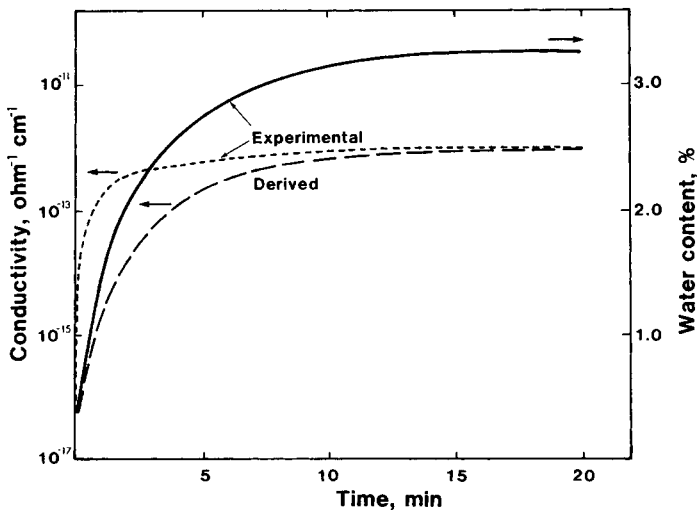


Fig. 5. The change in conductivity with time when a large step change in water pressure is introduced: initial moisture content 0%; vapor pressure change 0-5 Torr.

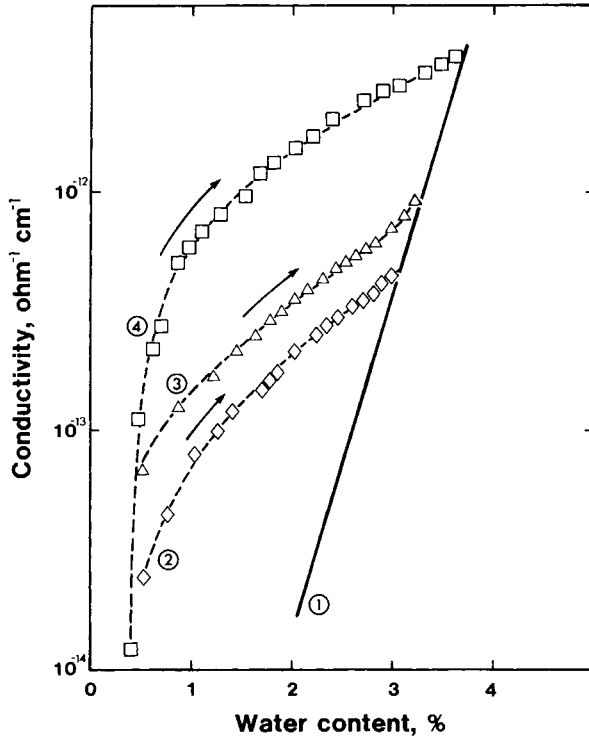


Fig. 6. Conductivity vs. moisture content. Plot now includes data obtained during unsteady-state conditions: (1) steady-state data; (2-4) unsteady-state data. Humidity steps: (2) 0-21%; (3) 0-23.5%; (4) 0-30.5%.

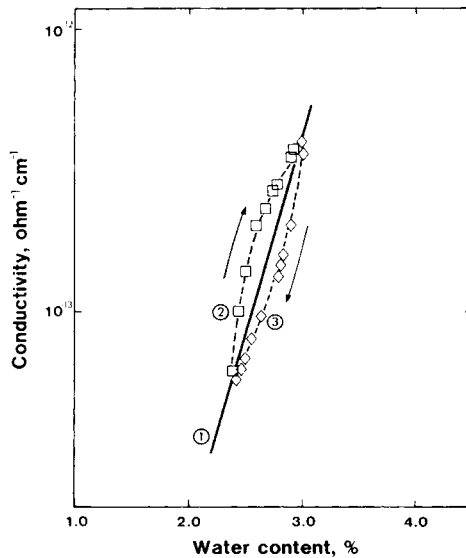


Fig. 7. Conductivity vs. moisture content during unsteady-state conditions: (1) steady-state data. Humidity steps: (2) 11.6-21% RH; (3) 21-11.6% RH.

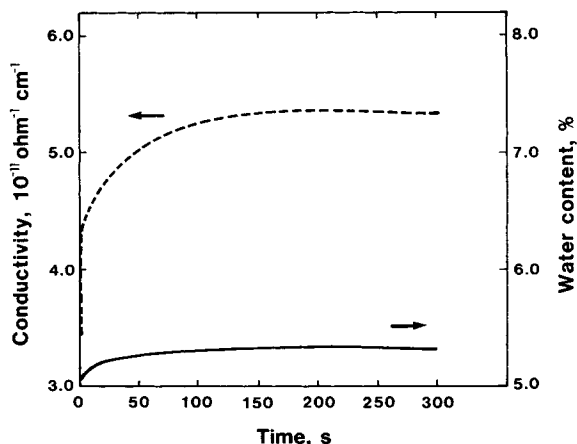


Fig. 8. The change in conductivity after step change in water vapor pressure. Initial moisture content 5%. Change in vapor pressure 8.5–9.8 Torr.

High Water Content, Small Humidity Step

Finally, Figure 8 is a typical curve for an experiment where the initial moisture content was at least 4–5%, and the step-change in water pressure was relatively small ($\sim 6\%$ RH). The initial response is almost instantaneous followed by a slow increase in conductivity.

Several effects were considered as being responsible for the difference between steady-state and transient conductivity.

Depletion of Charges from the Surface

During sorption of water some of the ions become mobile and move towards the electrodes, thus depleting charges from surface or near surface regions. For a first approximation we can assume that the time to reach current maximum (t_i) corresponds to the transit time of charges between the electrodes. The mobility of the charge carriers is

$$\mu = L^2/(Vt_i) \quad (3)$$

where V = applied voltage and L = interelectrode gap. Taking experimental values $t_i = 40$ s, $L = 3$ mm, and $V = 200$ V a mobility value $\mu = 1.0 \times 10^{-5} \text{ cm}^2/\text{V} \cdot \text{s}$ was obtained. This value is 3–4 orders of magnitude higher than that reported for the mobility of ions in cellulose¹⁸ and paper.¹⁹ Thus this effect cannot explain the observed peaks in current.

Effect of Water Diffusion

Upon establishment of a step change in vapor pressure, the water content at the surface quickly reaches its equilibrium value at that vapor pressure. A water concentration profile is thus established in the material. This acts as a driving force for the diffusion of water. The conductivity profile across the sample can be expected to reflect the water content profile. Thus, there is at or near the surface a zone where conductivity will be enhanced by the high water concentration, even though the overall (measured) water content

is still quite low. Therefore, for a given water content the conductivity under non-steady-state sorption, will be greater than the σ at steady state. While the above discussion may help to explain the results of Figure 5, it cannot account for the peak in Figure 3.

Thermal Effects

There are thermal effects associated with water sorption due to the heat of sorption. If heat is not dissipated at the same rate as it is generated, the sample temperature will increase. This effect is well documented for wool,²⁰⁻²² where temperature rises of up to 40°C have been measured for step change from 0 to 23.5 Torr.²³ While the heat of water sorption is higher for wool than for cotton,²⁴ the effect is the same. Since the electrical conduction is strongly temperature-dependent, a small change in the sample temperature may lead to large changes in conductivity. Thermal effects would be expected to predominate at low water content where sorption heat is largest. The peak observed in Figure 3 would seem to be attributable to such effects. The similarity between the curve of Figure 4 (peak height vs. water content) and the curve of the differential heat of sorption vs. water content⁸ confirms this.

Assuming that only thermal effects are present, it is possible to calculate from the data a theoretical temperature rise in the sample. Equation (4), simply derived from the Arrhenius relationship $\sigma = \sigma_0 \exp(-E/kT)$, expresses the temperature T as a function of the transient conductivity σ_t , the steady-state conductivity σ_s (at the same water content), and the activation energy E :

$$T = [1 - (kT_a/E) \ln(\sigma_t/\sigma_s)]^{-1} T_a \quad (4)$$

where T_a is the ambient temperature and k is the Boltzman constant.

Examples are presented in Figure 9 (for small humidity steps) and in Figure 10 (for large humidity steps), which correspond to curves 2,3, and 4 of Figure 6. For the calculations, a value of 1.33 eV was used for the ac-

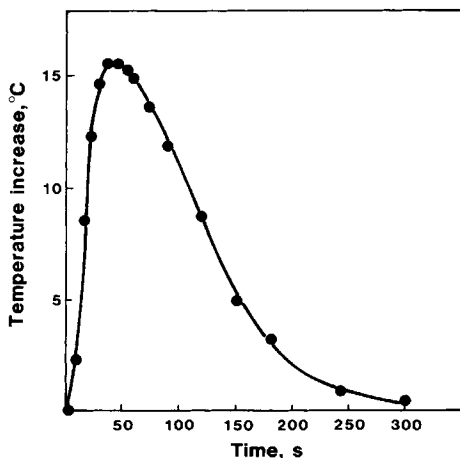


Fig. 9. Typical temperature increase after small step change in humidity is applied. Initial moisture content: 0%. Step change in vapor pressure is 0.15 Torr.

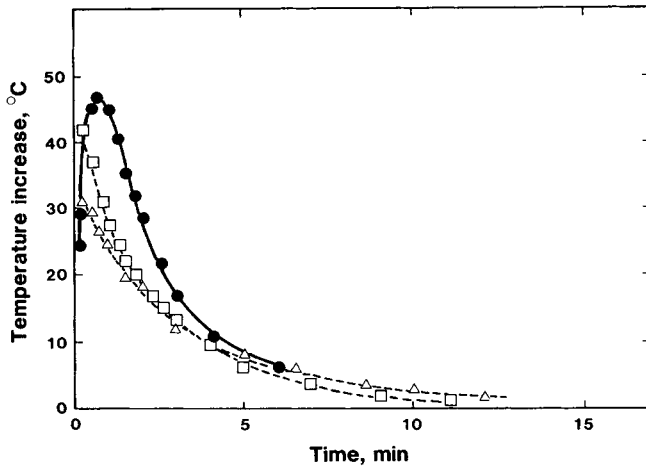


Fig. 10. Temperature increase after large humidity step is applied to dry sample: (●) 0-30%; (□) 0-23%; (△) 0-21%.

tivation energy.³ The activation energy does depend on water content, but, between 0% and 3.5% moisture content, it varies by only 20%.²⁵

Another example in Figure 11 shows the calculated temperature variation when the humidity was changed from 11% to 21% and back to 11% (experiment of Fig. 7). During desorption, the sample temperature decreases (water desorption is an endothermic process) and then increases slowly until ambient temperature is attained.

Surface Effects

The behavior shown in Fig. 8, where the initial response is quasiinstantaneous, can be explained if we assume that a layer of adsorbed water has formed at the surface and is much more conductive than the bulk of the fibre.

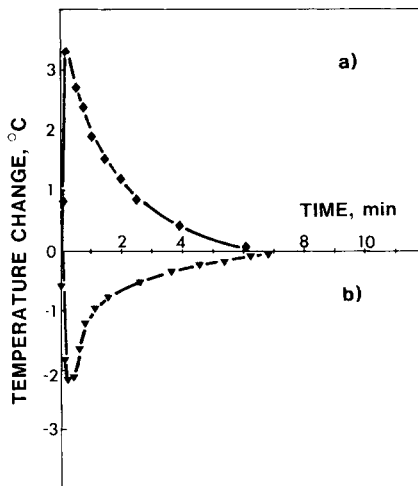


Fig. 11. Temperature variation during a step increase followed by a step decrease in humidity for a sample having 2.2% initial water content.

CONCLUSION

The difference between transient and steady-state values of conductivity at a given moisture content have been explained by thermal effects due to sorption heat. Other effects, related to the diffusion of water within the cellulose fibers may also be present, although they could not, alone, explain all the observed results. Further studies of the moisture dependence of electrical conductivity under transient conditions may contribute to a better understanding of the interaction between water and cellulose.

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