DIELECTRIC RELAXATION IN CELLULOSE CONTAINING SORBED VAPORS

A Thesis

by

Ruth Seidman, B.Sc.

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LIST OF SYMBOLS

A - $\dfrac{1}{1 + \left[2\pi f \tau \dfrac{\epsilon_0 + 2}{\epsilon_{\infty} + 2}\right]^2}$

C_g - geometric capacitance of dielectric cell

C_o - extraneous capacitance

D - electric displacement

E - electric intensity due to the applied field, potential across the dielectric

f - frequency of electric field

F - electric intensity acting on a molecule

$\Delta F^{\star}$ - free energy of activation

G - measured a - c. conductance

$G_{D.C.}$ - d - c. conductance

G_D - conductance associated with Debye effects

h - Planck's constant

$\Delta H^{\star}$ - enthalpy of activation

I - polarization, or electric moment per unit volume

k - Boltzmann's constant

k_o - molecular rate of relaxation

$K^{\star}$ - constant for the equilibrium between the activated complex and the reactants in a rate process

m - mean moment of a molecule

n - refractive index, number of dipoles contained in one cc.

N - Avogadro's number

P - molar polarization

Δr - position of the end of the quartz spiral relative to an arbitrarily chosen reference point

R - Nk

ΔS^{*} - entropy of activation

T - absolute temperature

T_m - temperature of maximum loss

V_2/V - volume fraction of paper in the dielectric cell

x - $\frac{\epsilon_0 + 2}{\epsilon_{\infty} + 2}\omega\tau$

z - $\left\{\frac{\epsilon''}{(\epsilon_0 - \epsilon_{\infty})}\right\}^2$

α - polarizability

α_0 - polarizability due to distortion

δ - $\tan^{-1} \frac{\epsilon''}{\epsilon'}$

ϵ - dielectric constant

ϵ' - real part of dielectric constant when expressed as a complex number

ϵ'' - dielectric loss factor

ϵ'_1 - dielectric constant of paper sheet

ϵ''_1 - dielectric loss of paper sheet

ϵ'_2 - dielectric constant of compound dielectric

ϵ''_2 - dielectric loss of compound dielectric

ϵ_0 - static dielectric constant

ϵ_{∞} - optical dielectric constant

$\epsilon''_{D.C.}$ - contribution to dielectric loss from d - c. conductance

ϵ''_{max} - maximum value of ϵ''

$(\epsilon''_2)_{max}$ - maximum value of ϵ''_2

Λ - specific d - c. conductivity of dielectric

μ - permanent dipole moment

ρ, d - density

σ - $\dfrac{\Delta(\log \tau)}{\Delta\left(\frac{1}{T}\right)}$

τ - relaxation time

ω - angular frequency

ω_{max} - experimentally determined angular frequency for maximum absorption.

TABLE OF CONTENTS

INTRODUCTION

This work is based upon a group of experiments planned to reveal certain effects of water and other hydroxyl-containing substances on dielectric relaxation in cellulose. It is, therefore, appropriate to begin with an exposition of the theoretical considerations underlying the fundamental Debye equations for the dielectric constant and loss as well as the relaxation time of a dielectric (13). It is relevant as well to consider Eyring's picture of dielectric relaxation as an activated rate process. Following this, pertinent aspects of the structure and general properties of cellulose will be traced (33). Finally, work done on the dielectric properties of this system will be reviewed.

Assuming the existence of a dielectric constant and confining attention to isotropic substances, the mean moment of a molecule, m, acted upon by a steady electric intensity F can be written:

$$m = \alpha F \qquad (1)$$

α is the molecular constant "Polarizability". In determining F, in addition to considering the electric intensity arising from the applied field, one must take due account of the reacting field as well as other related factors. The oldest problem, concerned with media composed of non-polar molecules, can now be regarded as settled; we still await a completely satisfactory treatment of the case where the molecules possess permanent dipoles (18). If one assumes that the molecules are moving totally independently of each other, one obtains the relation (13):

$$F = E + \frac{4\pi}{3} I \qquad (2)$$

where E is the electric intensity due to the applied field, and I is the polarization, or electric moment per unit volume. By definition,

$$I = nm = n\alpha\left(E + \frac{4\pi}{3} I\right) \qquad (3)$$

where n is the number of dipoles contained in one cc. Also by definition,

$$D = E + 4\pi I \qquad (4)$$

$$= \epsilon E \qquad (5)$$

where ϵ is the dielectric constant of the substance. From (3), (4), and (5), one obtains:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n\alpha \qquad (6)$$

The Molar Polarization P is defined:

$$P = \frac{4\pi}{3} N\alpha = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} \qquad (7)$$

where ρ is the density and M the molecular weight of the substance, and N is Avogadro's number. For polar substances whose molecules have a permanent dipole moment μ, the mean electric moment is expressed by:

$$m = \left(\alpha_0 + \frac{\mu^2}{3kT}\right) F \qquad (8)$$

T being the absolute temperature. The factor α_0 takes care of the distortion effect, the factor $\mu^2/3kT$ of the orientation effect. This contribution from orientation has been derived by the classical method employed by Debye (13), and, in addition, by the methods of wave mechanics (13), quantum mechanics (60), and the Born-Heisenberg mechanics (40, 45). Thus, summing over a discrete number of states in the newer methods has given the same average moment as averaging over a continuous distribution in the classical derivation.

For a periodic field of angular frequency ω the mean moment becomes complex and is given by:

$$m = \left\{ \frac{\mu^2}{3kT} \frac{1}{1 + i\omega\tau} + \alpha_0 \right\} F \qquad (9)$$

and the molar polarization P is expressed by:

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = P(\omega) = \frac{4\pi N}{3} \left\{ \alpha_0 + \frac{\mu^2}{3kT} \frac{1}{1 + i\omega\tau} \right\} \qquad (10)$$

The relaxation time τ is defined as the time in seconds for the variable part of the moment distribution function to be reduced to 1/e of its initial value after instantaneous removal of an electric field that has caused them to become oriented in a definite direction.

Two dielectric constants ϵ_0 and ϵ_{∞} are defined by:

$$\frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \frac{M}{\rho} = \frac{4\pi}{3} N \alpha_0 \qquad (11)$$

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \frac{M}{\rho} = \frac{4\pi}{3} N \left\{ \alpha_0 + \frac{\mu^2}{3kT} \right\} \qquad (12)$$

According to (10) the dielectric constant ϵ_{∞} denotes the value of ϵ for high frequencies -- the optical dielectric constant -- and ϵ_0 is the static dielectric constant, observed for $\omega = 0$.

The value of ϵ as a function of frequency is then given by:

$$\epsilon = \frac{\dfrac{\epsilon_0}{\epsilon_0 + 2} + i\omega\tau \dfrac{\epsilon_{\infty}}{\epsilon_{\infty} + 2}}{\dfrac{1}{\epsilon_0 + 2} + i\omega\tau \dfrac{1}{\epsilon_{\infty} + 2}} \qquad (13)$$

and can be written as:

$$\epsilon = \epsilon' - i\epsilon'' \qquad (14)$$

where:

$$\left.\begin{aligned} \epsilon' &= \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + x^2} \\ \epsilon'' &= \frac{\epsilon_0 - \epsilon_{\infty}}{1 + x^2}\, x \\ x &= \frac{\epsilon_0 + 2}{\epsilon_{\infty} + 2}\, \omega\tau \end{aligned}\right\} \qquad (15)$$

ϵ'' attains a maximum value when $x = 1$; upon this fact rests the method generally used for the determination of τ. In attempts to evaluate the internal field in polar liquids, Onsager and others have suggested that the factor $\epsilon_0 + 2/\epsilon_{\infty} + 2$ occurring in Debye's equations be replaced by unity (24). In the present work the relaxation time has been evaluated as $1/\omega_{max}$ where ω_{max} is the experimentally determined angular frequency for maximum absorption.

Thus, when measurements are made as a function of frequency at temperature T one obtains curves for ϵ' and ϵ'' as shown in Figure 1. Over a given range of frequencies ϵ' undergoes a rapid decrease and at the same time ϵ'' goes through a maximum in the form of a symmetrical bell-shaped curve. For these phenomena a correspondence law holds stating that any effect of the frequency can likewise be obtained at constant frequency by making a corresponding change in τ. In particular,

τ is markedly dependent on the temperature as well as the viscosity (13, 30, 35, 41). Consequently, it is not surprising that similar curves of ϵ' and ϵ'' are obtained when the frequency is kept constant and the temperature changed. Because of the greater ease of traversing a suitable temperature range than the corresponding frequency range the majority of workers in this field have chosen to change their variables in the former fashion. They have for the most part assumed that the value of the relaxation time obtained in this way from the maxima of the ϵ'' curves was the same as that obtained at this temperature at varying frequency. There are those who have questioned the validity of this assumption (27, 38), but their objections do not appear to be at all sound in principle. For example two workers (27) object on the grounds that to each temperature there corresponds a characteristic dipolar structure, i.e., a different substance. If the implication is that it is the viscosity which changes, then it is this very fact which is the basis for the phenomena observed, as shown above.

On the other hand, a very simple demonstration of the equivalence of the two methods is offered as follows (29):

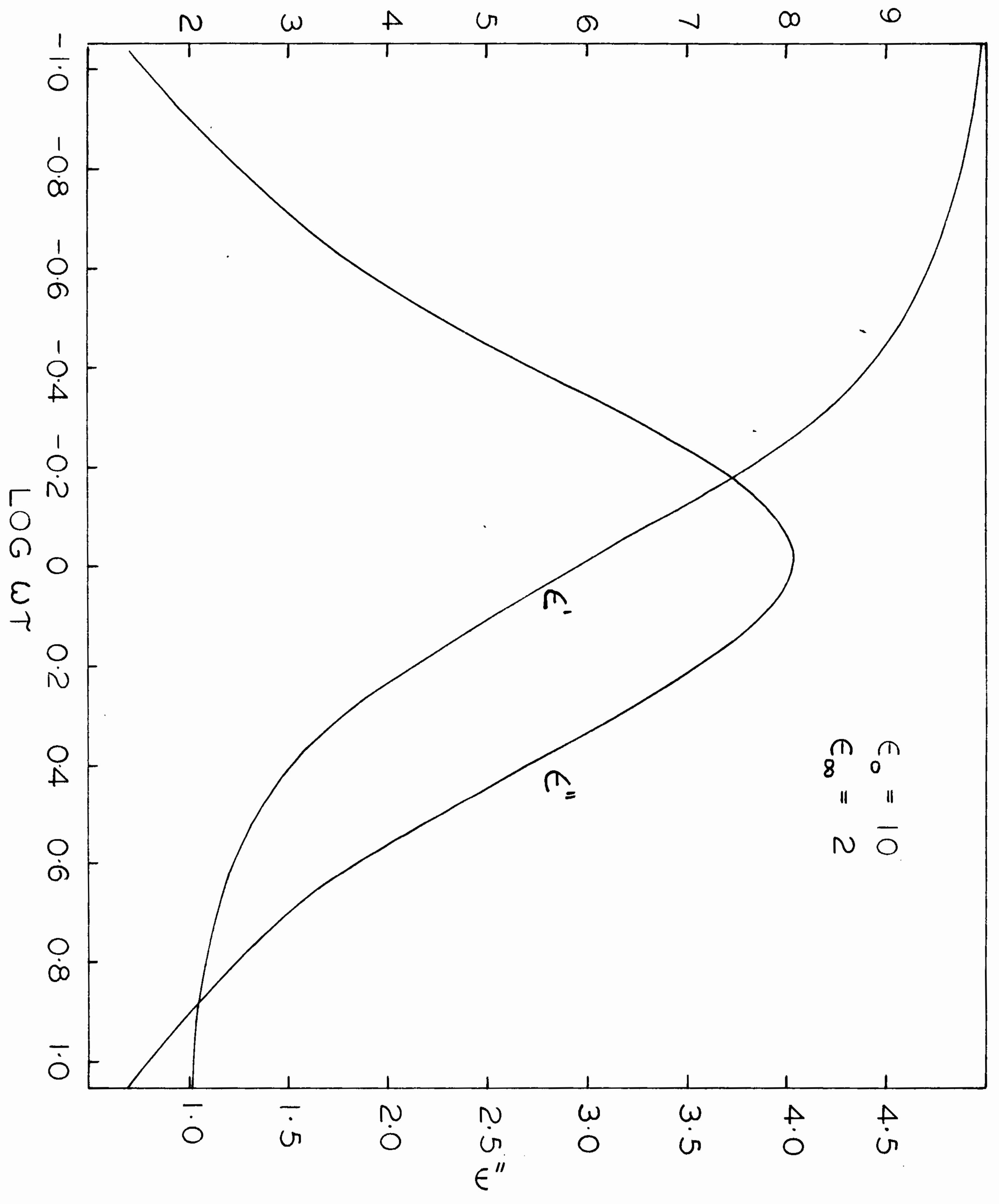
Let z $\quad = \quad \left\{ \dfrac{\epsilon''}{\epsilon_0 - \epsilon_{oo}} \right\}^2$

Put A $\quad = \quad \dfrac{1}{1 + \left[2\pi f \tau \, \dfrac{\epsilon_0 + 2}{\epsilon_{oo} + 2} \right]^2}$

According to Debye's theory $z = A - A^2$ (Equation 15). Since ϵ_0 and ϵ_{oo} are independent of f, the frequency of maximum loss f_m is given by

FIGURE 1

Variation of ϵ' and ϵ'' with log f in a dispersion region.



ε'
9
8
7
6
5
4
3
2
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
LOG ωT
ε''
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
ε'
ε''
$\epsilon_o = 10$
$\epsilon_\infty = 2$

$$\frac{dz}{df} = 0 = (1 - 2A)\frac{\partial A}{\partial f}$$

The temperature T_m which makes z a maximum is given by:

$$\frac{dz}{dT} = 0 = (1 - 2A)\frac{\partial A}{\partial T}$$

In each case the relaxation time τ is given by the unique equation $1 - 2A = 0$.

The equivalence of the two methods is apparent as well in the solid model representing tan δ ($= \frac{\epsilon''}{\epsilon'}$) as a function of both frequency and temperature for terylene (48).

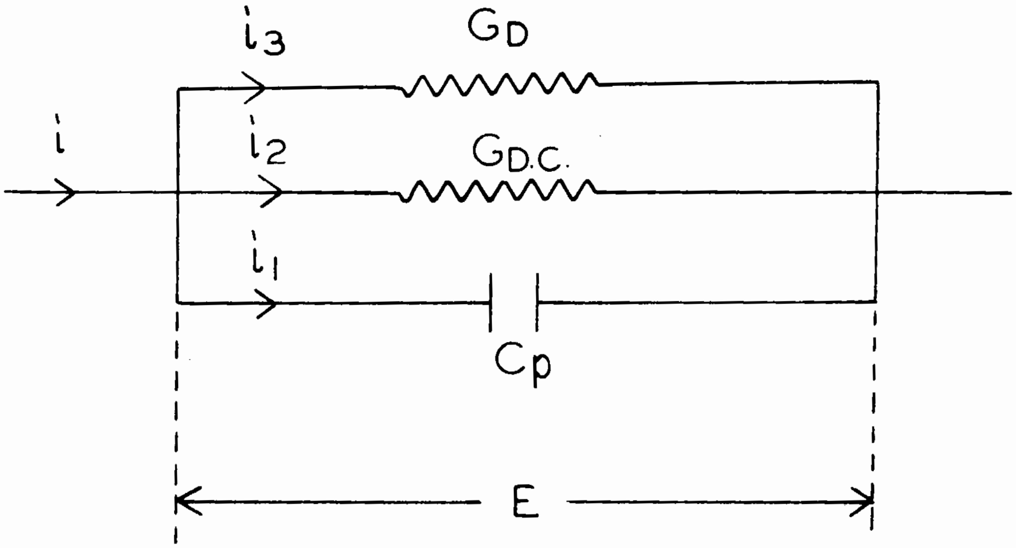
For a given field ϵ'' and ω are related in a very simple way to the rate of loss of energy from the electric field (20). ϵ'' may then be considered as a measure of this loss.

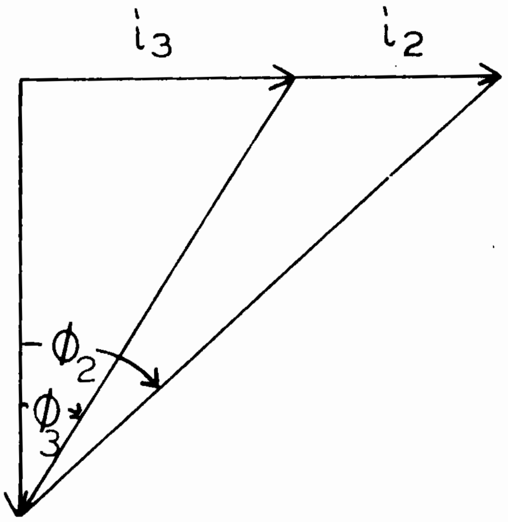
When a dielectric is a conductor as well, there is a contribution to ϵ'' which varies inversely as the frequency. Let the dielectric examined be represented by the model in Figure 2a, the phase diagram being shown in Figure 2b. C_p is the parallel capacitance, $G_{D.C.}$ the d-c. conductance, G_D the conductance associated with Debye effects; and i_1, i_2, and i_3 are the corresponding currents. ϕ, and ϕ_2 are the phase angles associated with G_D and $G_D + G_{D.C.}$, respectively. E is the potential across the dielectric. The model is then described by the following equations:

FIGURE 2

a) Model for a conducting dipolar dielectric.

b) Phase diagram for dielectric of Figure 2a.


i_3
G_D
i
i_2
$G_{D.C.}$
i_1
C_p
E


i_3
i_2
ϕ_2
ϕ_3

$$i_1 = E\omega C_p; \quad i_2 = EG_{D.C.}; \quad i_3 = EG_D$$

$$\epsilon''_D = \epsilon' \tan\phi_3 = \epsilon' \frac{i_3}{i_1} = \epsilon' \frac{G_D}{\omega C_p} = \frac{G_D}{\omega C_g}$$

$$\epsilon''_T = \epsilon' \tan\phi_2 = \epsilon' \frac{i_3 + i_2}{i_1} = \epsilon' \frac{G_D + G_{D.C.}}{\omega C_p} = \frac{G_D + G_{D.C.}}{\omega C_g}$$

$$\therefore \; \epsilon''_{D.C.} = \frac{G_{D.C.}}{\omega C_g}$$

For a parallel plate condenser

$$G_{D.C.} = \Lambda \frac{a}{l}$$

$$C_g = \epsilon_o \frac{a}{l}$$

where Λ is the specific d.c. conductivity of the dielectric and a is the cross-sectional area and l the length of the condenser. Therefore

$$\epsilon''_{D.C.} = \frac{\Lambda \frac{a}{l}}{\omega \frac{\epsilon_o}{100} \frac{a}{l}} = \frac{1000 \times 10^{11}}{8.85 \times 4\pi} \times \frac{4\pi\Lambda}{\omega}$$

$$= 9 \times 10^{11} \times \frac{4\pi\Lambda}{\omega}$$

This is the familiar expression (9) which is quite general for condensers of all shapes.

In the treatment leading to Equations 15, it was assumed that upon removal of an electrical field the molecule loses the impressed orientation by a succession of random movements, the trace of its original position becoming gradually less after each such movement. In the consideration of the process as a unimolecular reaction it was found more reasonable to assume that the dipoles change their orientation, not gradually, but in a series of sudden jumps. It was further assumed that the rate of jumping was equal to the molecular rate of relaxation k_o, where

$$k_o = \frac{1}{\tau} \qquad (16)$$

k_o being analogous to the specific rate constant of chemical reactions.

In the theory of absolute reaction rates (28) it is assumed that, in any atomic or molecular process whose rate is temperature dependent, the atoms or molecules involved must first come together to form what is called an activated complex. This is regarded as being situated at the top of an energy barrier lying between the initial and final states. It is supposed that the initial reactants are always in equilibrium with the activated complexes.

The simple expression for the rate constant of a temperature dependent process is derived to be:

$$k_o = \frac{kT}{h} K^{\bigstar} \qquad (17)$$

where $K^{\bigstar}$ is the constant for the equilibrium between the activated complex and the reactants, k is Boltzmann's constant, and h is Planck's constant. Writing $K^{\bigstar}$ in terms of the standard free energy of the process, $\Delta F^{\bigstar}$,

$$-\Delta F^{*} = RT \ln K^{*}$$

or

$$K^{*} = e^{-\Delta F^{*}/RT}$$

Whence (17) becomes

$$k_o = \frac{kT}{h} e^{-\frac{\Delta F^{*}}{RT}} = \frac{kT}{h} e^{\frac{-\Delta H^{*}}{RT}} e^{\frac{\Delta S^{*}}{R}} \qquad (18)$$

ΔH^{*} and ΔS^{*} are the standard enthalpy and entropy changes, respectively, which accompany the activation process. Equations (16) and (18) are combined to give

$$\frac{1}{\tau} = \frac{kT}{h} e^{\frac{-\Delta F^{*}}{RT}} \qquad (19)$$

From Equation (19) it is seen that the rate of the process is determined, not by the heat of activation ΔH^{*}, but by the free energy of activation ΔF^{*}. Hence, if a process is characterized by a large ΔH^{*}, it can still take place with rapidity if accompanied by a correspondingly large increase in entropy. On the other hand a small ΔH^{*} value does not imply a high rate if a small entropy term is involved.

It is of great interest to consider the implications of the values that can be assumed by ΔS^{*}. Many relaxation processes are characterized by large positive values of the entropy of activation, often higher than 100 e.u. For substances exhibiting such behaviour it is impossible not to conclude that more than one molecule is involved in the activation. This situation can be visualized as follows (38):

According to the current ideas on liquid structure the state of affairs in the immediate neighbourhood of a molecule approximates that in a crystal. Thus, in order to satisfy the requirements for stability in a normal state (where "normal" refers to a state represented by a local minimum on the potential energy surface for the system) the region in the neighbourhood of the molecule must be characterized by optimum packing, dipole orientation, hydrogen bonding (if such bonds are possible), etc. If a change is to occur in the orientation of the molecule so that its state will then be represented by a second minimum on the potential energy surface, the neighbouring molecules in the "crystal" must also undergo some change in order that the resulting configuration may again be stable. The process of activation can be easily visualized as involving a loosening of whatever bonds are holding the molecules together, so that the activated state approximates to that of a gas as far as intermolecular forces are concerned. This requires a large entropy increase comprised of the contributions of the members of the "crystal". From this activated state the molecules can go back to their original configuration or proceed to another stable one.

Thus, if the process of activation is regarded as essentially a vaporization, it is possible to calculate the number of molecules in the "crystal" defined above from the magnitude of ΔS^{*} and the entropy of vaporization of a single molecule as calculated from Trouton's rule. At about room temperature for a substance with a molecular weight of 100, each molecule undergoes a net entropy change of 10 to 15 e.u. during the "vaporization". Consequently it can be concluded that anywhere up to 10 or more molecules can be vaporized in each activation process. Thus, the magnitude of ΔS^{*} in Eyring's equation gives rise to the conclusion that, in general, more than one molecule is involved in the activation process of dielectric relaxation. The same conclusion may be drawn from the value of f obtained from the modified Arrhenius expression for the rate constant of a process:

$$k_o = c_1 \frac{e^{-(A/RT + f)} \left[\frac{A}{RT} + f\right]^{f}}{f!}$$

f has been written for Hinshelwood's (n/2 - 1), where n is the number of quadratic terms in which activation energy is shared. n is given by $n = 3a - 6$, "a" being the number of atoms in the molecule, so that f is limited by the value of a. Frank calculated the value of f = 140 for the dielectric relaxation of cetyl palmitate dissolved in paraffin wax. From this high value, one cannot help but conclude as before that the relaxation process involves several neighbouring molecules as well as the central one under consideration (17).

Other evidence supporting this view is presented as follows. In a binary system of two polar substances one would expect anomalous dispersion to occur over two frequency ranges corresponding to two relaxation rates. Such an effect has actually been observed for certain systems, but its appearance depends upon concentration as well as other factors (51). In other systems, e.g. polyvinyl chloride plasticized with varying amounts of tricresyl phosphate, a single dielectric loss maximum is observed.

In agreement with the views of Schallamach this suggests that it is no longer correct to speak of the relaxation of single dipoles, but that larger regions must be considered (38).

Values of ΔS^{*} not far removed from zero ($+ .79$ e.u. $> \Delta S^{*} > - 2$ e.u.) have been interpreted as indicating that the molecules of the substance concerned are free to rotate without involving breaking of bonds to neighbours. Such behaviour is shown by the hexasubstituted benzenes (66). On the other hand, negative values of ΔS^{*} varying from $- 3$ to $- 5$ e.u. were found for several substances (65); it was thought unlikely that these negative values arose from experimental errors. In other words, the authors felt that these values were significant, but at the time made no statement concerning their physical import. However, others (26, 47) are of the opinion that the absolute rate equation is not sufficiently accurate for an absolute significance to be placed upon the negativity of such small values. That is, the liquids involved are to be considered as merely more mobile than substances characterized by more positive values of ΔS^{*}. This view is probably a very wise one, for it must be borne in mind that the liquids involved (toluene, o-xylene, p-cymene, etc.) were especially chosen for their very small dipole moment in order that they might be regarded as dilute solutions of dipoles in a non-polar medium. Thus, the activation process would involve much less bond-breaking in these cases than for the associated liquids usually investigated. Hence it is not surprising that their values for ΔS^{*} extend into negativity, especially if no absolute significance is to be placed upon them.

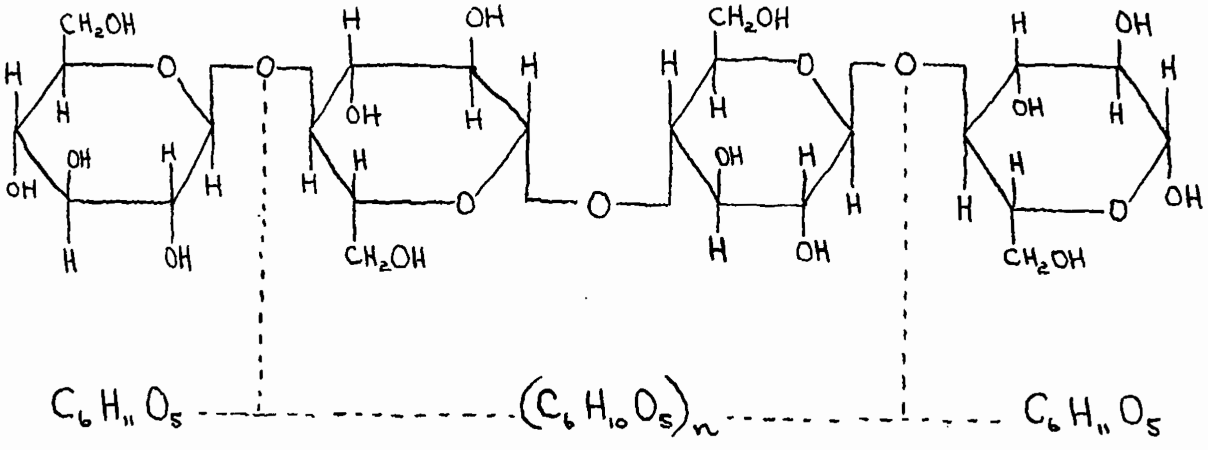
It is of interest to introduce the results obtained with the same substance dissolved in solvents of different degrees of structural order. Entropies of activation were calculated for solutions of dioctyl phthalate in both polystyrene and polythene. It is well known that, as compared to polystyrene, polythene is much more closely packed in structure, largely owing to its crystallinity. One would consequently expect the necessity for a greater disorganization, hence a greater increase in entropy, for activation in polythene. The results obtained are recorded below; they are in agreement with expectation (42).

dioctyl phthalate in polythene	33	e.u.
dioctyl phthalate in polystyrene	- 2	e.u.

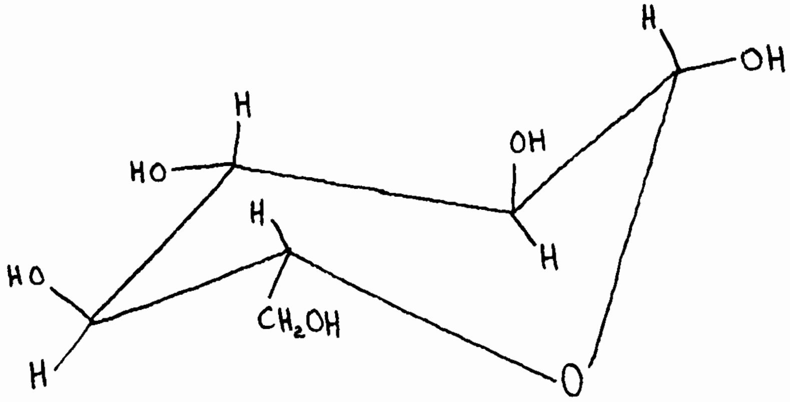
Work on multicomponent dielectrics has proceded in two general directions. There are those who have with more or less success attempted to assign values of dielectric constant and loss to a particular component (3, 36, 37, 39, 44, 49). Then there are the others, including the present author, who, while making measurements as a function of composition, have nevertheless persisted in considering the system as a whole in this respect.

Investigations have been made on rubber swollen in turn in various polar and non-polar solvents (52). From measurements at a constant frequency it was found that in all cases the temperature of maximun loss due to rubber was shifted in varying degree to lower temperatures by an increase in concentration of swelling agent. On the other hand the loss maxima of the solvents were brought by the rubber to much higher temperatures than those of the pure liquids. In all cases the enthalpy of activation for rubber relaxation decreased with increasing concentration of swelling agent, which may, therefore, be considered as having a plasticizing action on the rubber. A similar effect was produced as well in polyvinyl chloride by tetralin (23), diphenyl (22), and tricresyl phosphate (11), and in polycaproamide by adsorbed water and methanol (21). On the other hand the vulcanization of rubber with increasing amounts of sulphur (38, 53) is reflected in regularly increasing enthalpies and entropies of activation for relaxation. This is in agreement with the view that the sulphur introduces added rigidity by formation of bridges between chains.

Native cellulose consists of molecules having a degree of polymerization of at least 3000 (33). What may today be regarded as the established constitution of a single molecule is represented in the following formula:



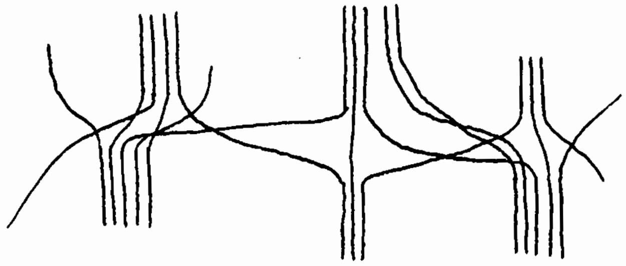
The two terminal members of a chain are differentiated from all others by the possession of four instead of three hydroxyl groups; one of these groups to the extreme right of the figure is distinguished by its aldehydic character. Each chain member possesses one primary group. A consideration of spatial conditions makes it plain that chains extending in one direction (such as must largely constitute a fibre) can only be built up by continuous 1-4 glucosidic linkages from the frame of β glucose in the armchair form, shown below.



In a straight portion of the chain, the centres of gravity of the atoms of the ring are distributed over two parallel planes. The hydrophobic H atoms are above and below these planes and laterally there are the hydrophilic OH groups. An arrangement of such chains in a crystal is thus easily visualized, the "secondary valences" of the hydroxyl groups being taken up in the fairly powerful hydrogen bonds.

The picture of cellulose fibre structure centres around the concept of micellae, the meaning of which has undergone a subtle change from the time, 70 odd years ago, when C.v. Nageli coined the term (33). They are now considered as statistically distributed regions of a latticed order in a mass of substance consisting of approximately parallel chain molecules.

The "crystalline" regions alternate with less well-ordered "amorphous" regions, somewhat as shown below, there being no connection between the linear extension of the micellae and the length of the chains.



In the process of water sorption the water penetrates between the molecular chains into the fine, and even finest amorphous regions, but does not reach the core of the crystalline regions. Now if the molecular chains are aligned in the direction of the fibre, the fibre will swell transversely only, but not longitudinally, in accordance with the observed behaviour of well-oriented cellulose fibres. The sorption process is now regarded as one of solution, so that a cellulose fibre containing sorbed water may be considered as an arrangement of more or less regularly alternating regions of crystalline mycellae and of amorphous material in solution in water.

The phenomenon of hysteresis may, after Urquhart (46), be considered as a consequence of this random arrangement of mycellae: After drying, the cellulose molecules try to attain positions such that there is the greatest possible mutual satisfaction of secondary valences. Because of the relative immobility of the long molecules, it is not possible for them to reach the arrangement of true minimum potential energy.

If the fibre is again brought into contact with water vapor, the fibre molecules try to come into as complete a contact as possible with the water molecules; that is, they tend to become independent of each other. However, in consequence of the inertia-like effect just mentioned, the positions of the cellulose molecules at the same relative humidity are, after drying, less favorable to taking up water than before. In other words, the fibre behaves on desorption like a material with a higher amount of amorphous region. The fraction of amorphous region in native fibres has been determined as 0.30 by X-ray methods, this being in good agreement with values derived from sorption and density data (32, 34).

Throughout this work the term "adsorbed vapor" is used to distinguish the vapor uptake on the adsorption side of the sorption isotherm from that on the desorption side.

A fundamental problem arises whenever an absolute measurement of the dielectric constant of cellulose is desired. This is inherent in the fibrous structure of the material, the porous nature of which must be circumvented in some manner if one wishes to avoid the necessity of taking into account anomalous surface effects. Two methods, quite simple in principle, have been developed to this end -- the technique of liquid mixtures and the pressure method.

The technique of liquid mixtures was first used by Starke (55) and independently by De Luca, Campbell, and Maass (15). These authors showed that the problem of the porous spaces in cellulose could be solved by filling them with a liquid having the same dielectric constant as the cellulose itself. The method involves finding a liquid mixture which is isodielectric with the cellulose. The composition of this liquid mixture was the point of intersection of two liquid-composition versus dielectric constant curves, one with and one without the cellulose sample in place in the condenser. The dielectric constant of a liquid of this composition was then determined directly, or from a curve showing the relation between percentage composition and dielectric constant. The major uncertainty in this method, arising from the small angle at which the curves crossed, was neatly resolved by Brown (7) by simply plotting differences in dielectric constant due to cellulose rather than the composite values.

An entirely different approach was employed by Deleventi and Hansen (16) and later by Calkins (8). They constructed the electrodes of their condenser in such a way that pressure could be applied to the cellulose sample up to a point where it no longer had any effect on the measurements. At this point it was assumed that the pores in the sample had been effectively eliminated.

Data obtained by these workers will be reviewed in the discussion.

Dielectric dispersion in dry cellophane was discovered by Stoops in 1934 (57); this was attributed to typical dipole orientation. Analysis of his data shows no significant difference in the values of the relaxation time τ whether calculated from data obtained at constant temperature, or, on the other hand, at constant frequency. There is no reason why this should not also be the case for other forms of cellulose.

Because of the softening action of water on cellulose it was reasonable to assume that sorbed moisture facilitates dipole rotation and thus appropriately shifts the position of maximum absorption. Some data was available on this subject but the results appeared contradictory.

Dakin and Auxier (10) measured the dielectric constant and dissipation factor of commercial papers as a function of frequency at 28°C. When observable, the frequency of maximum absorption was unaffected by the moisture content. Similar measurements by Henniger (31) at -5°C. for paper with moisture contents of 0 and 5.6% gave the same general results.

On the other hand Veith measured the dissipation factor of paper at different moisture contents as a function of temperature over the range -40 to 40°C. at fixed frequencies (61). The temperature of maximum loss, observed only at the highest experimental frequency, 100 Kc., appeared to decrease with increasing moisture content.

In view of this conflicting evidence further investigation appeared desirable. It was decided to work with a purified form of cellulose in order to eliminate effects due to high loss impurities. The working frequencies chosen were such that absorption regions appeared in the temperature range -60 to 45°C.

EXPERIMENTAL

Electrical Apparatus

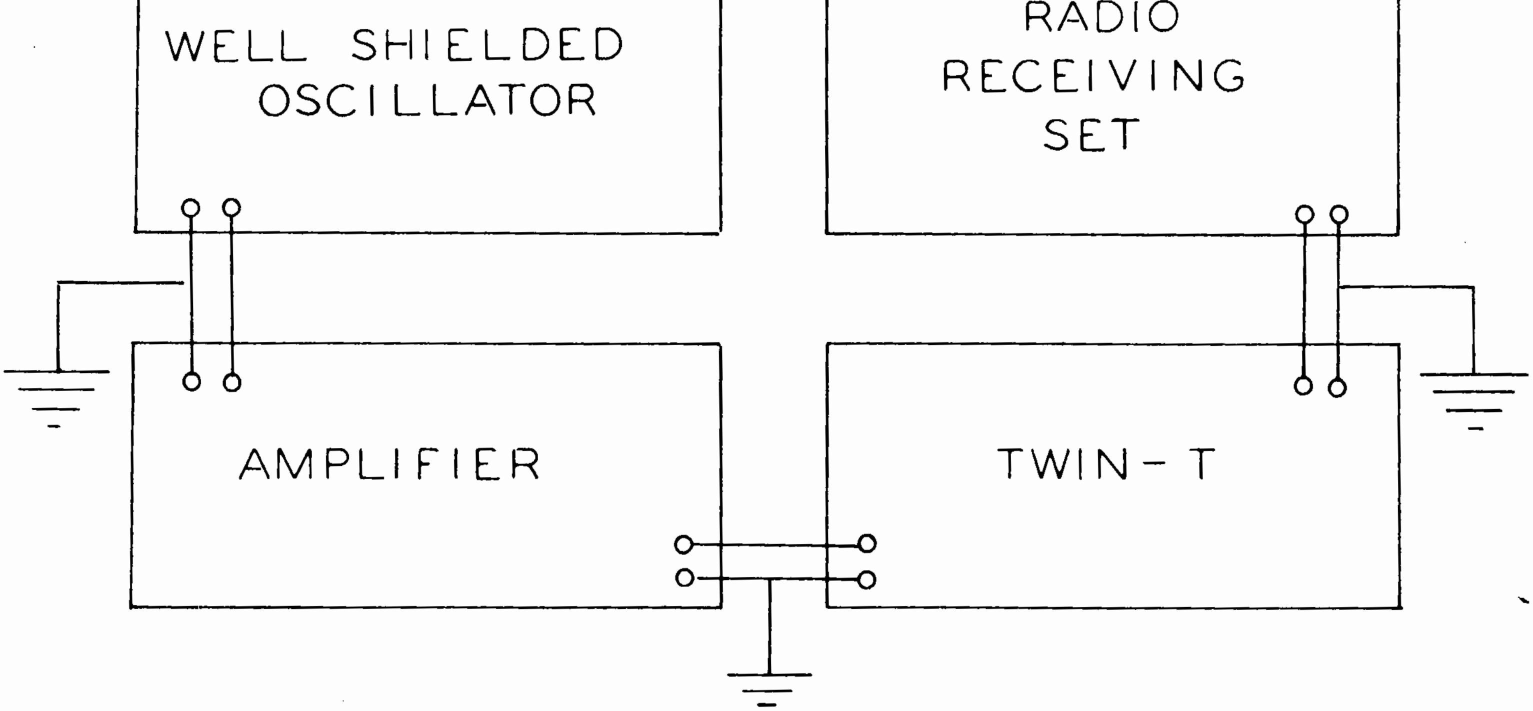
For the frequency range of 10 Kc. to 1 Mc. covered in this work, two measuring circuits used previously in this laboratory (24, 25) were employed. These were the General Radio Company's Type 821-A Twin-T Impedance measuring circuit and the Type 716-C Schering bridge.

The Twin-T circuit together with auxiliary equipment was employed at 1 and .55 Mc. The arrangement and method of operation were essentially the same as that used previously, the circuit being shown in Figure 3. The appropriate high-frequency signal generated by the oscillator was amplified and then fed into the Twin-T circuit. In the absence of balance conditions in this circuit part of the carrier signal entered the radio receiver. An internal beat oscillator in the receiver was employed to produce beats with the carrier signal. This heterodyne signal was amplified and could be heard through earphones plugged into jacks in the receiver. On balancing the Twin-T circuit, the signal no longer entered the detector and no sound could be heard.

At 200 and 100 Kc. the Schering bridge was employed. The appropriate signal was fed into the bridge from the same oscillator-amplifier arrangement used with the Twin-T circuit; the method of null detection was likewise the same. In this case the null detector was the RCA Victor Type T.E.-236-B Radio Receiving Equipment consisting of a Power Unit, MI-22102, and a Receiver Unit, MI-22112.

FIGURE 3

Twin-T circuit and auxiliary apparatus.


WELL SHIELDED OSCILLATOR
RADIO RECEIVING SET
AMPLIFIER
TWIN - T

This equipment could detect signals in the range 15-600 Kc. The Power Unit was carefully designed in order to maintain an accurate calibration of the receiver and a high degree of frequency stability. The Receiver Unit was completely shielded both internally and externally to minimize cross-talk between receivers. Filters were provided which increased the effective CW selectivity and improved the signal-to-noise ratio. C.W. reception and improved sensitivity and selectivity was accomplished by the use of a specially designed autodyne detector circuit. This detector employed the familiar electron coupling with the resultant minimizing of reaction in all circuit switching in the audio system. A very high degree of frequency stability is inherent in this type of circuit which renders it possible to obtain the desired performance characteristics of this detector without critical adjustment of the controls. These were set as follows:

With the "Frequency Band" switch set at the appropriate frequency range, the "Tuning" control was adjusted until the desired signal was heard. The "Regeneration" control was set so that the detector was oscillating as evidenced by a double click heard in the headphones when the "Osc. Test" button was pressed and released. The "Sensitivity" control was set at 6; this gave the required sensitivity without overloading the receiver with noise. The "Antenna Trimmer" and "RF Trimmer" controls were kept in the same position for both frequencies, while the "AVC" and "Audio Tuning Off-On" switches were at all times kept in the "Off" position.

The Schering bridge was likewise employed for the measurements at 30 and 10 Kc., the auxiliary equipment and general arrangement of the circuit being essentially similar to that employed previously (24). The bridge was energized by a Hewlett-Packard No. 200A Audio Oscillator. The oscillator signal was fed to the bridge and thence through a Hewlett-Packard Model 404A vacuum tube voltmeter amplifier circuit to a 5-in. Sylvania cathode ray oscilloscope which served as null detector. The method of null detection was a simplification of that employed previously. The signal, which was applied to the "y" plates of the oscilloscope was beat against an appropriate internal oscillation applied across the "x" plates. This resulted in a wave-form on the oscilloscope screen the amplitude of which was reduced to zero upon balancing of the bridge.

Thus, the principle of operation of all three arrangements is effectively the same. In each case the reference for measurement is the condition of zero energy transfer across the measuring circuit. In each case the residual signal transferred across the unbalanced circuit is beat against an internal oscillation in the null detector. On the one hand the resultant electrical oscillation is transformed to an audible sound wave, on the other hand it becomes a visible electron wave.

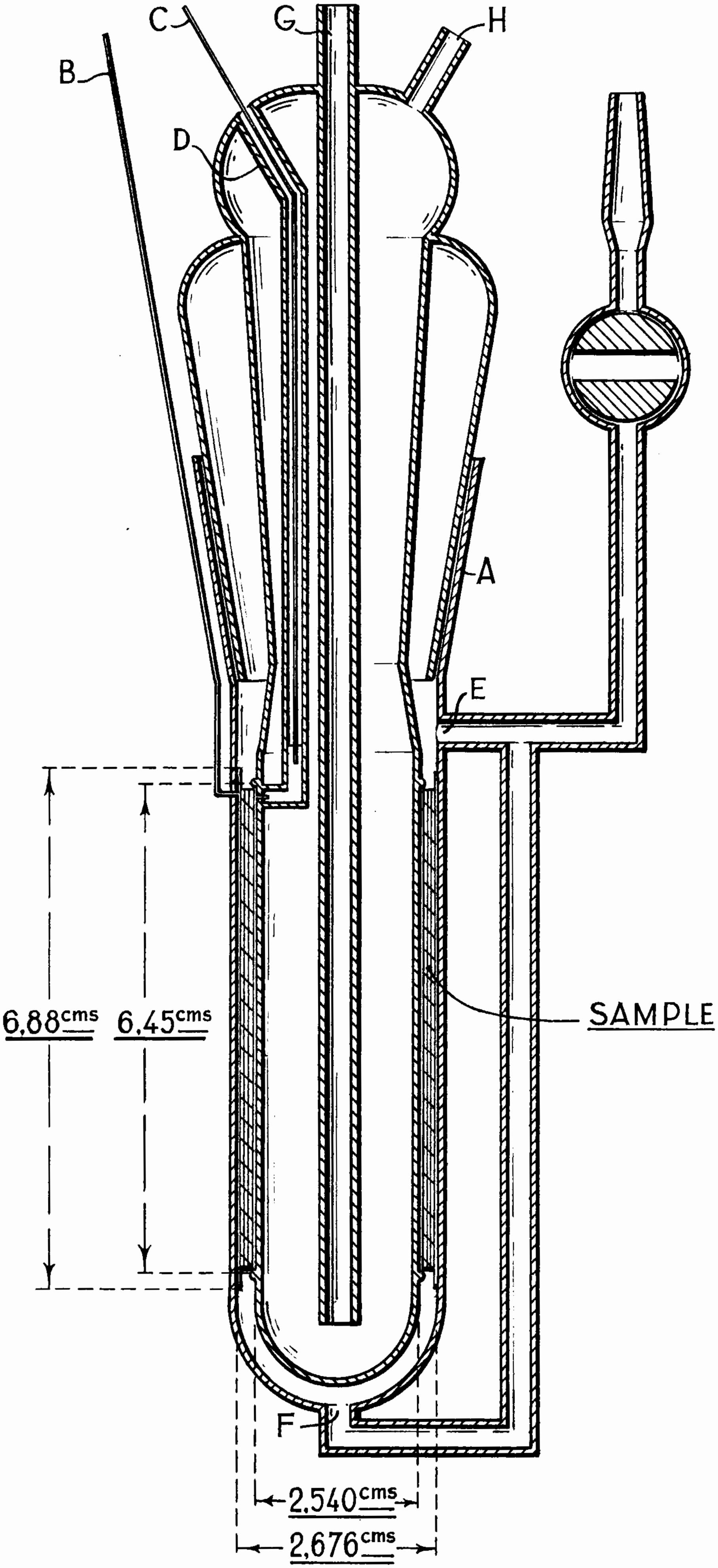
D-c. resistance measurements were made with a General Radio Type 1861-A Megohmmeter. With few exceptions to be mentioned below, there was no appreciable contribution to the measured a-c. losses (see Introduction).

Dielectric Cell

It was necessary to design a cell in which the vapor content

<u>FIGURE 4</u>

Dielectric cell.


C
G
H
B
D
A
E
6,88 cms
6,45 cms
SAMPLE
F
2,540 cms
2,676 cms

of the cellulose sample could be systematically varied.

The arrangement employed (Figure 4) consisted of a pair of concentric Pyrex glass cylinders connected at a standard-taper ground-glass joint A. On the glass wall at each side of the annular space three layers of platinum were deposited; these constituted the electrodes. Contact was made to copper wires B and C on the outside by thin pieces of platinum sealed in the glass. The copper wire C dipped into mercury at the bottom of the tube D, the mercury making contact with the platinum sealed in the glass. Connection to the conditioning system was made both above and below the electrode deposit at E and F in order to accelerate diffusion of vapor throughout the cellulose sample. Four tiny blebs of glass were sealed both above and below the electrode on the inner cylinder to serve as spacers for the sample. Two tubes G and H were to make provision for circulation of thermostatted liquid through the inner cylinder; no necessity was found for this application of the tubes.

Such cells, in which metal electrodes are deposited on glass, were introduced by Sayce and Briscoe in 1925, and have since been used with success (5, 12, 58). Because of the small coefficient of thermal expansion of glass, cells of this type have no appreciable temperature coefficient of capacity. Thus, there was effectively no variation in capacitance of the cell over the 80-degree range covered in this work.

Connection of the cell to each measuring circuit was made by immersion of the copper leads B and C (Figure 4) in mercury contained in small tubes, to the bottom of which the leads from the measuring circuit were sealed with Glyptal cement. These leads were two copper wires, 13 in. long B. and S. No. 20 guage, kept about one inch apart by three narrow pieces of lucite. The connecting mercury tubes were mounted on a masonite board which also served to support the cell.

The cell was calibrated with dry benzene at 25.0°C. Assuming the value of 2.274 for the dielectric constant of benzene at this temperature (6), the geometric capacitance (Cg) was found to be 68.0 $\mu\mu$f., while the extraneous capacitance (C_0) including leads was 9.7 $\mu\mu$f.

In the case of the Schering bridge the dielectric constant, ϵ'_2, and dielectric loss, ϵ''_2, were determined by the substitution method as follows:

$$Cx = \Delta C \tag{1}$$

$$Dx = .01\frac{C'}{\Delta C}\frac{f}{f_0}\Delta D \tag{2}$$

$$\epsilon'_2 = \frac{C_x - C_o}{C_g} \tag{3}$$

$$\epsilon''_2 = \epsilon'_2 D_x \tag{4}$$

ΔC and ΔD are the bridge readings and Cx and Dx the actual values of the parallel capacitance and dissipation factor of the unknown. C' is the capacitance reading with the unknown disconnected, f_0 is the frequency setting of the range selector switch, and f the working frequency. The simplicity of equations (1) and (2) results from the fact that in no case in this work was the measured dissipation factor of the unknown greater than 0.1.

In the case of the Twin-T circuit it was necessary to correct the capacitance reading ΔC for the lead inductance L, in order to obtain the true capacitance C_x, the relation among which is expressed in:

$$\frac{1}{\Delta C} = \frac{1}{C_x} - \omega^2 L_1 \qquad (5)$$

where ω is the angular frequency of measurement. L_1 was obtained from a plot of $1/\Delta C$ versus ω^2 as 9.9×10^{-7} h. on the basis of two independent determinations for the empty cell and for the cell filled with benzene. The value of the internal lead inductance of the precision condenser did not contribute appreciably to L_1.

Equation (5) defines the correction factor associated with L_1 as follows:

$$\gamma = 1 + \omega^2 L_1 \Delta C \qquad (6)$$

Values of γ for varying ΔC at .55 and 1 Mc. are presented in Table I.

The unknown capacitance was then given by:

$$C_x = \frac{\Delta C}{\gamma} \qquad (7)$$

the dielectric constant being obtained from Equation (3).

No other corrections of this nature were found to be necessary. The conductance G was obtained by subtracting from the measured value a small amount equal to the value for the empty cell. The dielectric loss was calculated from this as follows:

$$\epsilon'' = \frac{G(f/f_0)^2}{\omega C_g} \qquad (8)$$

where f_0 is the nominal switch-position frequency and f the frequency of measurement.

TABLE I

Correction Factor γ for lead inductance

ΔC	γ	
	.55 Mc.	1 Mc.
70	1.001	1.003
80		
90		1.004
100		
110		
120		1.005
130	1.002	
140		1.006
150		
160		
170		1.007

Materials

The cellulose investigated was a sample from Schleicher and Schuell No. 589 Red Ribbon quantitative filter paper of an extra dense quality, with a reported ash content of 0.007%. Microscopic examination of the paper indicated it to be a rag furnish containing 75% bast fibre and 25% cotton. The analysis was as follows:

α-cellulose	98.4%
pentosan	1.1%
cupriethylene diamine viscosity	15.7 centipoises

Saturated salt solutions to be used for conditioning the paper at different water contents were prepared from the following reagents:

1) Lithium chloride -- Baker's Analyzed, C.P. Grade
2) Potassium acetate -- Eimer & Amend, C.P. Grade
3) Magnesium chloride -- Merck, Reagent Grade
4) Potassium carbonate -- Merck, Reagent Grade
5) Magnesium nitrate -- Merck, Reagent Grade
6) Ammonium sulphate -- Merck, Reagent Grade
7) Ammonium phosphate -- Merck, Reagent Grade

Absolute ethanol from the Canadian Industrial Alcohol Company, Limited was dried according to the method of Lund and Bjerrum (43). The reaction mixture was used as a source of dry vapor, the density of the distillate at 25.00 ± .05°C. being .7852 compared with .7850 reported by Lund and Bjerrum.

The sample of methanol used was dried in the same way as the ethanol.

Method

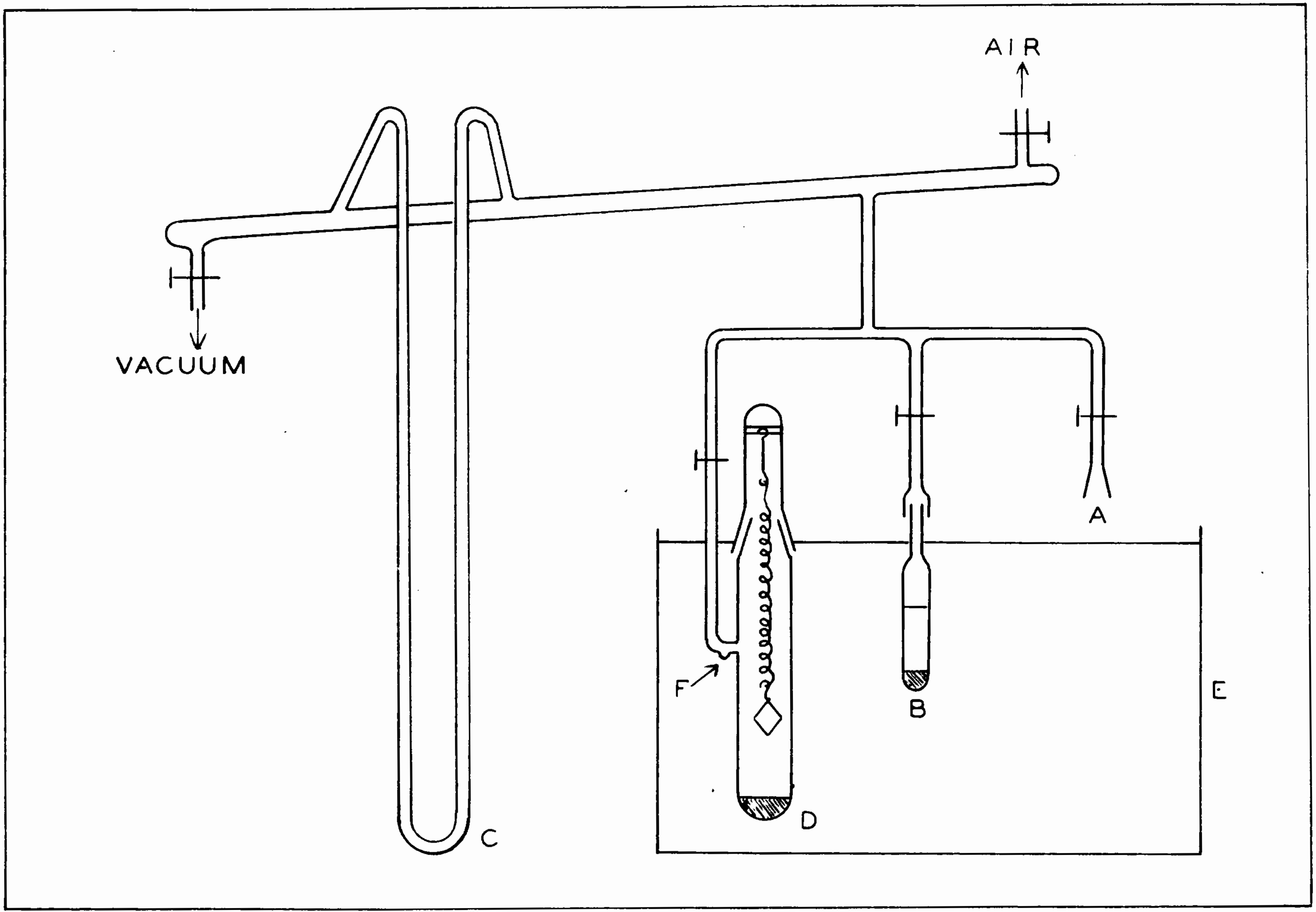
A simple system shown in Figure 5 provided the means of equilibrating the paper in the cell at different vapor contents. The dielectric cell was connected at A. B contained the vapor source, while the equilibrium vapor pressure was measured to 0.1 mm. with the U-tube mercury manometer C. The vapor content in each case was determined to less than 0.1 percent using a quartz spiral mounted in the sorption cell D. Both cells and the vapor tube were thermostatted at 25.00 ± .05°C. in the same water bath E. The buoyancy of the large sorption cell in the water was counteracted by mercury.

The quartz spiral, having a diameter of 5/8 inch, was capable of supporting 100 mg. with a sensitivity of from 0.1 mg. to 0.01 mg. The percentage vapor content of a 103 mg. sample of paper suspended from the spiral by a small platinum hook was determined by the corresponding percentage change in length of the spiral using a cathetometer reading to ± 0.03 mm. This corresponded to an error of less than 0.1 mg. Hooke's law was obeyed within the accuracy of measurement over the range covered.

The reference from which all measurements were made was the clearly defined bottom of the projection at F, while the extension of the spiral was determined by the position of the top of the platinum hook. These two readings were always taken for each measurement. The difference Δr was -17.68 mm. for the spiral and platinum hook. With the dry paper suspended Δr was 27.60 mm. so that the extension of the spiral due to the dry paper was 17.68 plus 27.60 equal to 45.28 mm.

FIGURE 5

Conditioning system.


AIR
VACUUM
A
B
C
D
E
F

Water

A strip of paper was tightly wrapped around the inner cylinder of the dielectric cell between the spacers and held in place by means of Glyptal cement. The cell with the paper fitting snugly into the annular space was assembled and connected to the conditioning system, through which it was evacuated with a Cenco Hyvac pump over a period of 20 hours to bring the sample to dryness. The result was dry paper as defined in this work, although there presumably remained a small residual amount of water which required more drastic methods for removal (33).

As a matter of fact, it is possible to estimate this residual from data obtained by Wahba on the heat of wetting of standard cellulose (63, 64). During the course of experiments planned to determine optimum conditions for drying, it was found that the heat of wetting for standard cellulose dried in vacuo for 15 hours at 25°C. is 9.7 cals./gm. dry material. This corresponded to a moisture content of 0.4%, which is probably the value of the residual in the dry sample of this work.

A series of dielectric measurements (described below) was then carried out.

The cell was then reconnected to the conditioning system and filled with vapor from the potassium acetate solution, forty-eight hours being allowed for equilibrium to be established. At this point the cell was disconnected and dielectric measurements carried out as before. This procedure was then repeated for each of the other salt solutions. The criterion for moisture equilibrium of the paper was the constancy of the equilibrium vapor pressure as well as of the extension of the quartz spiral, the paper on which was subjected to the same experimental conditions of temperature and relative humidity as the paper in the dielectric cell.

After equilibration at each moisture content a series of dielectric runs was carried out at each of several different frequencies over a temperature range of -58°C. to 26°C. The dielectric cell was immersed in a dewar flask filled with toluene. Using a small Variac-controlled heater, the temperature was raised to 26°C. at the rate of one degree per minute. After the cell was allowed to come to thermal equilibrium, appropriate readings of capacitance and dielectric loss were taken. The bath was then cooled with dry ice and readings were taken at regular intervals at successively lower temperatures down to -58°C. For each reading a cooling period of from six to eight minutes was provided, and an additional ten minutes was allowed for the cell to reach thermal equilibrium. The temperatures were read on a toluene thermometer, the ice point of which was found to be correct within experimental error. After reaching the lowest temperature the frequency was changed and similar measurements were made at increasing temperatures.

Thus, some of the runs were performed by going up the temperature scale, other by going down. By determining a complete cycle at a single frequency, it was shown that there was no temperature hysteresis, i.e., the direction of temperature change had no effect on the readings taken. The run performed at the first frequency was always repeated at the end of the series for a particular vapor content, and in all cases was found to be reproducible. Some slight exception to this generalization was found in the work with methanol and ethanol, and will be described in the next section.

With dry paper a marked temperature hysteresis was observed. This resulted from the low thermal conductivity in the evacuated cell. When dry nitrogen was admitted this effect disappeared without changing the measured capacitance at room temperature. The nitrogen (and in other instances the water vapor) thus served as the necessary heat conductor.

Measurements with the cell, emptied of paper, and filled with water vapor at the highest pressure employed in the work on dielectric relaxation showed that the variation of electrical properties was negligible with respect to temperature and to water vapor pressure.

Before equilibrating the paper in the cells at a given vapor content, it was necessary to remove from the vapor source any dissolved gases which might be adsorbed by the paper in addition to the vapor in question. This was accomplished in some cases by simple evacuation, and in others by a process of repeated freezing, evacuation, and melting, as described by Archer (1).

Methanol and Ethanol

In the experiments with methanol and ethanol it was necessary to avoid exposure of the stopcocks in the conditioning system to alcohol vapors for the weeks necessary for a complete run (50). Furthermore, since methanol (50) and presumably ethanol cannot be completely removed from cellulose by evacuation at room temperature, it appeared desirable to use as reference for the measurements not only the paper in a dry condition but when containing these tightly held portions of alcohol as well. The following modifications of the above procedure were accordingly adopted.

Methanol vapor was admitted to the conditioning system at a pressure of 60 mm. and allowed to remain in contact with the previously dried paper for two hours. The system was then evacuated over a second period of two hours. This process was repeated twice, the final evacuation being extended over a period of twelve hours. At this point the methanol content was 1.7%. After a series of dielectric measurements was performed as described above, the paper was conditioned to a methanol content of 2.5% and a further series of dielectric measurements performed. The paper was then subjected to a further process of alternate methanol conditionings and series of dielectric measurements up to a methanol content of 7.0%. Before each conditioning air was admitted to the system to permit regreasing of stopcocks, after which evacuation was carried out over a period of twelve hours, as before. With one exception, the amount of tightly bound methanol determined after the evacuation was always reproducible within experimental error.

After the experiments on methanol were completed, this residual was removed as follows. Water vapor was admitted to the system at 100% R.H. and allowed to remain in contact with the paper for several hours. The system was then evacuated over a period of 15 hours, the whole process being repeated once. In this way 85% of the residual methanol was removed, so that there remained an amount equal to 0.2% by weight of the dry paper.

The paper was then conditioned to an ethanol content of 8.5%, after which dielectric measurements were performed, as usual. Evacuation of the system for six hours left 2.3% residual ethanol none of which was removed after a subsequent evacuation lasting 14 hours. Dielectric measurements were performed at this ethanol content as well as at 4.6 and 6.9% ethanol. Before each of the latter conditionings, air was admitted to the system, this being followed by evacuation over a period of twelve hours, as in the case of methanol.

Altogether, three samples of paper were employed for the dielectric measurements in the course of this work. Sample #1 was used for the preliminary measurements on water, #2 for the major work on water, while #3 was used for the work on methanol and ethanol. The relaxation data to be discussed later were reproducible, but slight differences were found in the absolute values of dielectric constant and loss. These can partly be accounted for on the basis of corresponding differences in sample size, and will in fact be discussed below in the section on the analysis of the dielectric. The dimensions of the samples and the dielectric cell as well as the appropriate volume fractions are presented in Table II. It is observed that the geometric capacitance of the dielectric cell calculated from the cell dimensions is in good agreement with the value determined experimentally.

TABLE II

Sample dimensions and volume fractions in dielectric cell

Sample #	Length (ins.)	Width (ins.)	Thickness (ins.)	Volume (cc.)	Weight (gm.)	Density (gm/cc.)	Vol. Fraction in cell
1	8.85	2.63	.0063	2.40	1.251	.521	.630
2	8.91	2.59		2.38	1.182	.496	.625
3	8.88	2.64		2.42	1.202	.496	.635

Diameter of Outer electrode = d_o = 1.051 ins.
Diameter of inner electrode = d_i = .994 ins.
Length of Outer electrode = l_o = 2.71 ins.
Length of inner electrode = l_i = 2.54 ins.

$$\text{Volume of interelectrode space} = \frac{\pi l_i}{4}(d_o + d_i)(d_o - d_i)$$

$$= 3.81 \text{ cc.}$$

Geometric cap. of cell (calc.) = 64.4 $\mu\mu f$.

(exptl.) = 68.0 $\mu\mu f$.

RESULTS

Water

1) Preliminary

Preliminary results were obtained with a dielectric cell used previously in this laboratory (25) which had not been designed to be air-tight. Shifts in the position of the dispersion region for identical runs on successive days were as high as 20°C. At the same time distortion of the shape of the loss curve was observed, the magnitude of the effect varying from day to day. This was traced to varying amounts of moisture condensing on the bakelite insulation between the condenser plates during a run. This in turn was caused by corresponding changes in the relative humidity of the air on successive days, the best curves being obtained at lower relative humidities. Experiments performed on the empty cell showed that the maximum variation in loss could approach values observed for the cell filled with paper. The spurious results obtained were at once explained by the change in electrical properties with moisture content of the bakelite insulation as well as of the paper itself.

This early work suggested the feasibility of seeking a correlation between the shift in position of the dispersion region in paper and the amount of sorbed water it contained. The air-tight design of the dielectric cell of Figure 4 made it suitable for this purpose. Moreover, there was no danger of spurious results due to hygroscopic insulation, as the condenser plates were positioned solely by the ground-glass joint situated well above the upper boundary of the plates.

Data was obtained at 1000 Kc. for paper containing water adsorbed at 9 different relative humidities over the whole range; this is presented in Figures 6a and b. The dielectric constant ϵ'_2 is expressed in terms of the measured capacitance, $\Delta C = \gamma (C_o + \epsilon'_2 \, C_g)$, and the dielectric loss in terms of the a-c. conductance $G = \omega C_g \, \epsilon''_2$, the symbols having the significance stated earlier.

As expected, the dispersion region is shifted to lower temperatures by an increase in relative humidity. The maximum in the loss curve becomes an inflection point somewhere in the range 45 to 65% R.H., and finally disappears completely, so that the curve assumes an exponential form (Figure 6b). Associated with this is a marked increase in the slope of the dielectric constant curve, the effect being more pronounced at higher temperatures.

In fact, at 97 and 100% R.H. the form of this curve is that of two straight lines meeting at a point. One might be tempted to assume that these points of intersection represent a phase transition of the adsorbed water from ice to water. In such a case one would expect the intersection to correspond to a higher temperature with increase in relative humidity. Since the opposite is, in fact, the case, one must seek elsewhere for an interpretation of the phenomenon. If one assumes the sorption process to be one of solution (see Introduction) and assumes as well the validity of the Clausius-Clapeyron equation, then the ice point for adsorbed water occurs below the temperature range of investigation at relative humidities below 45%, the region of major interest in this work (61). In this region then one would not expect the results to be complicated by the occurrence of a phase transition of this nature.

If it is assumed that the fractional d-c. loss is the same for paper as for the compound dielectric studied here it is impossible to explain the high temperature rise in the loss curve in terms of ionic conductance. An appreciable d-c. contribution to the loss (less than $1\frac{1}{2}\%$ of the total) appears only at a R.H. of 97%, while the high temperature increase in loss is observed already at 65% R.H. Resolution of this problem on the basis of high temperature dispersion was likewise impossible in the present work, since the experimental arrangement ruled out performance of the necessary measurements at temperatures higher than the range investigated.

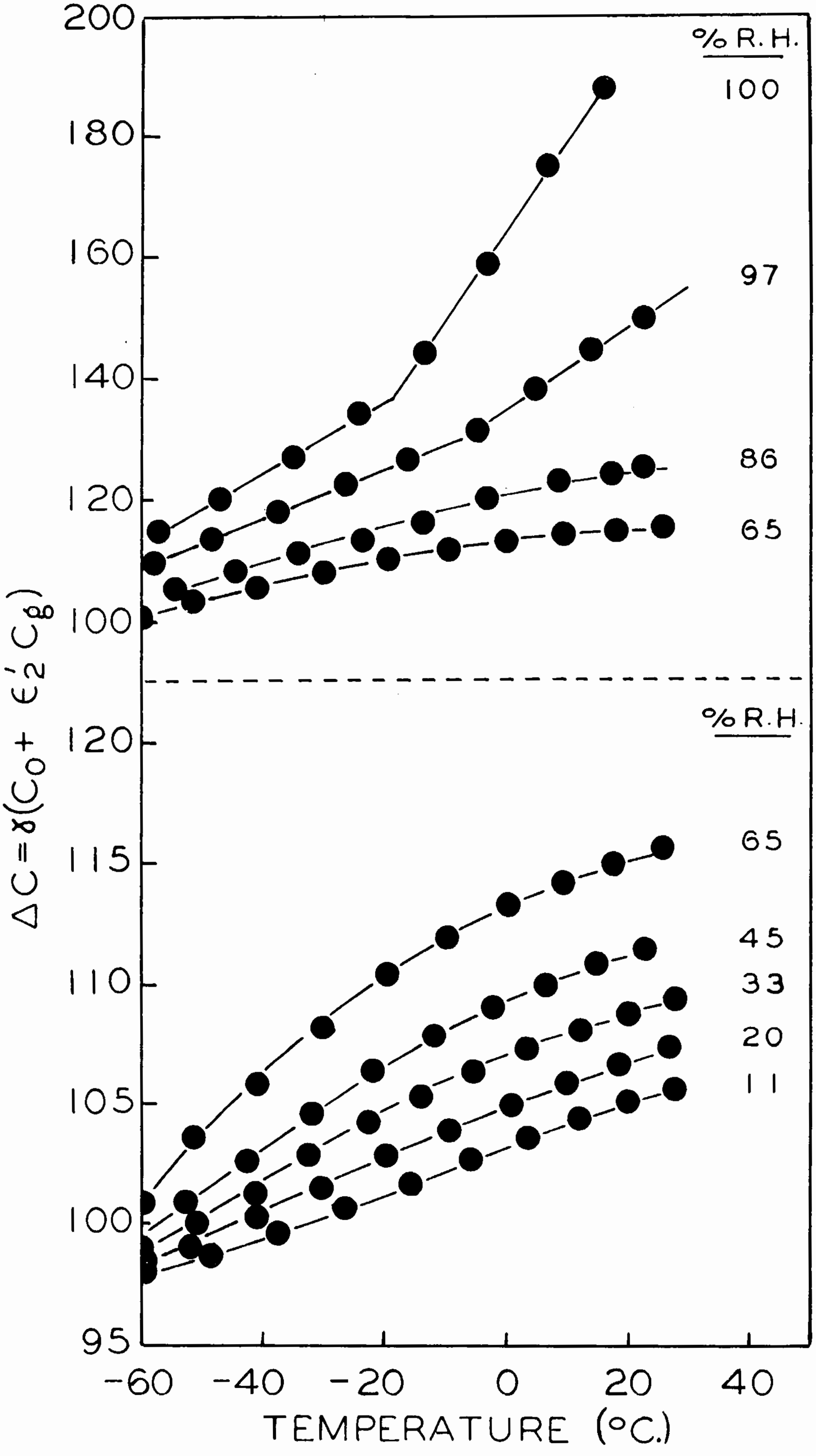
It was interesting to determine experimentally whether the shift in the position of the dispersion region was a function of moisture content or of relative humidity. Results on paper conditioned at 45% R.H. by both adsorption and desorption are presented in Figures 7a and b. It is apparent that the results are not a function of relative humidity alone.

The desorption curves correspond to a higher moisture content than those for adsorption, this being apparent from the increased dielectric constant and loss as well as the disappearance of the loss maximum. This points to the moisture content as the appropriate variable to be observed in the study of the dispersion region shift. This is in agreement with the fact that the d-c. resistance of cellulose likewise depends directly on its moisture content (46).

FIGURE 6

a) Effect of adsorbed water on the dielectric constant of paper at 1 Mc.

b) Effect of adsorbed water on the dielectric loss of paper at 1 Mc.



% R.H.
100
97
86
65
% R.H.
65
45
33
20
11
200
180
160
140
120
100
120
115
110
105
100
95
-60
-40
-20
0
20
40
TEMPERATURE (°C.)
$\Delta C = \gamma(C_0 + \epsilon_2' C_g)$

The results reviewed above represent the preliminary stage of this work and in minor respects are slightly in error. For example, all the dielectric runs were started at the low temperature end of the range investigated. The dielectric properties obtained in this way were considerably lower at the low temperatures than those obtained by the improved procedure described earlier, and the effect was most marked at the highest moisture content. This proved to result from condensation of water from the paper on to the walls of the cell as it was immersed in the bath, and yielded spurious results. However, the position of the loss maximum was unaffected by this effect, since, at the frequency of 1 Mc. employed at that time, the temperature of maximum loss was presumably high enough for the paper already to have come to equilibrium with the moisture in the cell by the time the maximum in the loss curve was attained.

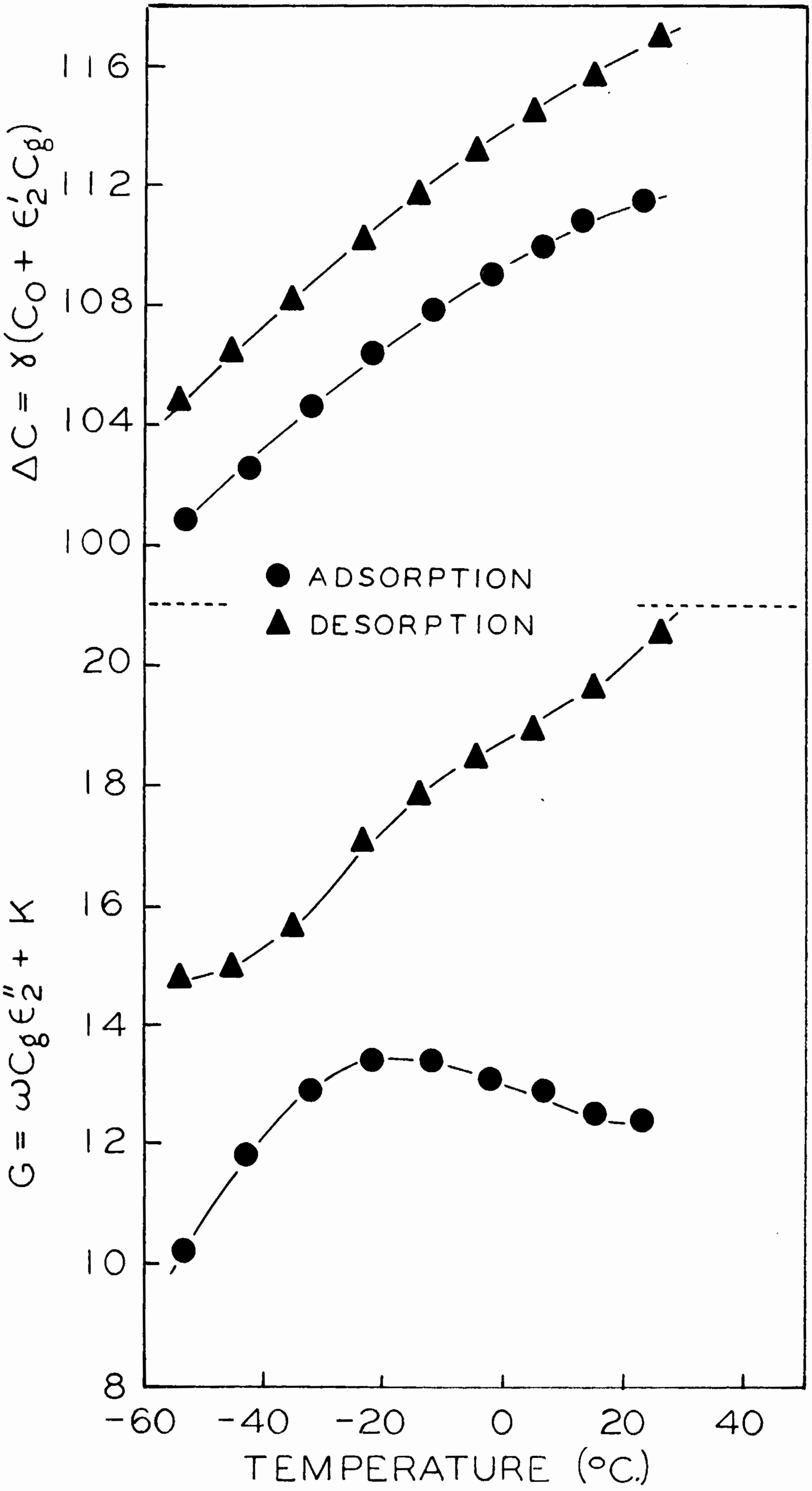
2) Results

The water sorption isotherm at 25°C. of the paper used in this work is shown in Table III and Figure 8. The adsorption branch lies a little above the corresponding curve of Wahba (64) for standard cellulose at 30°C. Removal of the residual of 0.4% (see Experimental) from the sample of paper used in this work would make this difference more obvious. This is a good check on the method used here for determining sorption. One would expect the same sorption isotherm in both cases, since the water uptake of cellulose has been shown to be a function of the fraction of amorphous substance, which is the same for all forms of native cellulose (33).

FIGURE 7

a) Effect of sorption hysteresis on the dielectric constant at 1 Mc. of paper conditioned at a relative humidity of 45%.

b) Effect of sorption hysteresis on the dielectric loss at 1 Mc. of paper conditioned at a relative humidity of 45%.



$\Delta C = \gamma(C_O + \epsilon_2' C_g)$
116
112
108
104
100
● ADSORPTION
▲ DESORPTION
$G = \omega C_g \epsilon_2'' + K$
20
18
16
14
12
10
8
−60
−40
−20
0
20
40
TEMPERATURE (°C.)

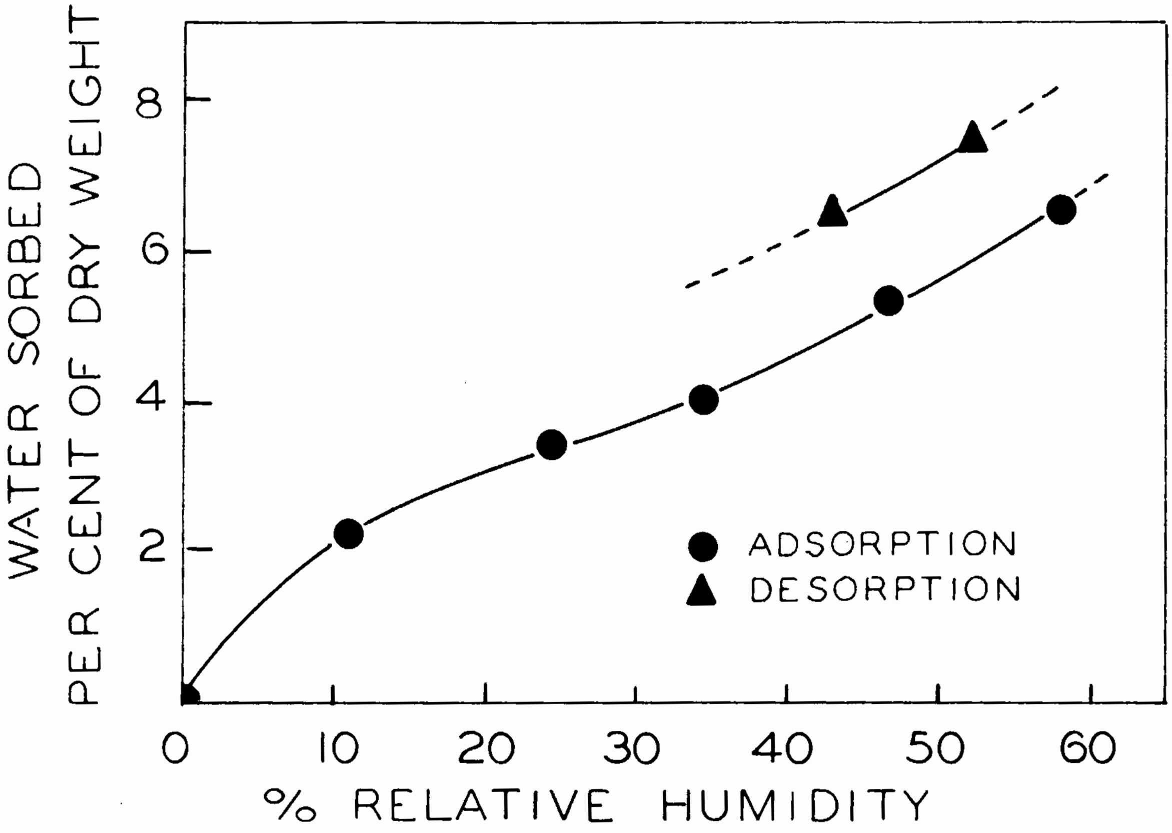
TABLE III

SORPTION OF WATER AT 25.0°C

Rel. Vap. Pressure	Water Sorbed per cent of Dry Weight
Adsorption	
0.0	0.0_0
10.9	2.2_5
24.4	3.4_4
34.4	4.0_2
46.6	5.3_4
58.0	6.5_8
95.8	17.6_7
Desorption	
52.1	7.4_9
42.8	6.4_9
0.0	0.0_0

FIGURE 8

Water sorption isotherm of paper at 25.0°C.



WATER SORBED
PER CENT OF DRY WEIGHT
8
6
4
2
0
10
20
30
40
50
60
% RELATIVE HUMIDITY
● ADSORPTION
▲ DESORPTION

The measured electrical values are expressed in terms of the dielectric constant and loss, ϵ'_2 and ϵ''_2, of the multiple layers of paper as arranged in the dielectric cell. ϵ'_2 is equivalent to the term "dielectric value" employed by Tausz and Rumm (59) and Brown (7). The expression of ϵ'_2 and ϵ''_2 in terms of the corresponding values for the paper as well as the cellulose fibre itself will be discussed later.

Results were obtained for water contents over the range 0 to 5.3% at frequencies from 30 to 1000 Kc. These are presented as a function of temperature in Tables IV to VII and Figures 9 and 10. Upon examination of the data certain salient features are observed at once.

The temperature coefficient of ϵ'_2 is everywhere positive. At the same time absorption regions occur at the temperatures T_m where ϵ''_2 passes through a maximum, $(\epsilon''_2)_{max}$. At a particular moisture content, a decrease in frequency causes a shift of T_m to lower temperatures, as well as a corresponding increase in ϵ'_2 at a particular temperature. These effects of varying frequency are shown for dry paper in Figure 11, and are qualitative indications of dielectric relaxation due to dipole orientation according to Debye theory (13).

The presence of moisture in the paper produced interesting variations in the data. First of all one notes the increase in ϵ'_2 often observed previously (3, 7, 14, 59, 61). This follows logically from the high static dielectric constant of water, 80, compared with 6 for cellulose. In agreement with Veith the effect is more pronounced at the higher temperatures. This is no doubt a reflection of the presumption that the maximum effect is observed in the case of the static dielectric

TABLE IV

Dielectric Dispersion of Dry Paper at 1000, 550, 100, 30 and 100 Kc.

1000 Kc.			550 Kc.			100 Kc.			30 Kc.			10 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.322	.0154	26.5	1.266	.0089	-56.0	1.297	.0082	-55.3	1.346	.0047	26.2	1.297	.0108	-55.4
1.310	.0160	14.6	1.277	.0106	-42.8	1.286	.0097	-42.1	1.341	.0059	14.3	1.309	.0111	-42.7
1.301	.0160	4.8	1.286	.0120	-31.6	1.297	.0107	-31.3	1.333	.0071	2.6	1.319	.0102	-31.4
1.291	.0152	-7.7	1.295	.0134	-19.8	1.307	.0109	-20.3	1.326	.0090	-9.2	1.326	.0089	-20.5
1.281	.0140	-19.4	1.304	.0143	-7.3	1.318	.0103	-7.7	1.318	.0110	-21.3	1.333	.0076	-8.3
1.274	.0124	-30.6	1.313	.0144	4.3	1.325	.0093	2.5	1.307	.0114	-32.6	1.341	.0063	4.2
1.264	.0105	-42.9	1.322	.0138	14.8	1.333	.0077	12.7	1.298	.0110	-43.4	1.346	.0043	15.4
1.257	.0084	-56.5	1.331	.0125	26.4	1.339	.0063	22.6	1.286	.0102	-55.7	1.352	.0036	25.7

TABLE V

Dielectric Dispersion of Paper containing 3.3% adsorbed water at 1000, 550, 100, 30 and 10 Kc.

1000 Kc.			550 Kc.			100 Kc.			30 Kc.			10 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.399	.0178	25.6	1.304	.0149	-54.5	1.321	.0139	-55.6	1.435	.0103	25.2	1.352	.0154	-55.4
1.387	.0197	13.7	1.318	.0177	-42.7	1.338	.0153	-42.9	1.428	.0099	13.9	1.369	.0149	-43.4
1.372	.0211	2.5	1.335	.0194	-30.9	1.358	.0157	-31.8	1.418	.0107	2.8	1.387	.0134	-31.5
1.362	.0215	-5.2	1.353	.0205	-19.2	1.373	.0147	-21.1	1.409	.0123	-8.2	1.402	.0117	-20.3
1.352	.0218	-13.6	1.370	.0201	-7.8	1.388	.0135	-10.0	1.397	.0138	-18.6	1.412	.0105	-9.6
1.342	.0213	-20.7	1.384	.0186	3.2	1.400	.0118	0.5	1.381	.0154	-30.8	1.422	.0099	0.8
1.328	.0204	-31.6	1.399	.0166	14.0	1.411	.0102	10.7	1.362	.0169	-43.6	1.429	.0094	11.6
1.312	.0178	-43.9	1.407	.0151	24.3	1.418	.0093	19.4	1.341	.0165	-56.0	1.439	.0100	22.8
1.294	.0150	-55.8												

TABLE VI

Dielectric Dispersion of Paper containing 4.0% adsorbed water

at 1000 Kc.

	1000 Kc.	
ϵ'_2	ϵ''_2	Temp.
1.420	.0202	20.7
1.407	.0216	9.0
1.396	.0227	-0.1
1.381	.0233	-11.1
1.368	.0233	-19.7
1.353	.0230	-29.5
1.336	.0217	-41.1
1.316	.0190	-55.7

TABLE VII

Dielectric Dispersion of Paper containing 5.3% adsorbed water at 1000, 100, 30 and 10 Kc.

1000 Kc.			100 Kc.			30 Kc.			10 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.453	.0234	20.4	1.363	.0197	-56.0	1.390	.0209	-56.5	1.534	.0349	29.0
1.444	.0241	10.2	1.391	.0201	-43.4	1.416	.0206	-43.6	1.516	.0269	18.5
1.427	.0250	-1.0	1.424	.0189	-27.4	1.440	.0186	-31.0	1.501	.0216	7.7
1.412	.0260	-12.6	1.447	.0169	-11.3	1.459	.0171	-18.6	1.487	.0177	-3.1
1.403	.0262	-22.6	1.462	.0161	-0.2	1.473	.0167	-6.9	1.473	.0161	-13.7
1.373	.0258	-34.8	1.473	.0162	9.4	1.485	.0183	3.8	1.461	.0156	-24.2
1.349	.0243	-46.4	1.482	.0173	19.0	1.499	.0203	14.2	1.444	.0165	-34.6
1.332	.0225	-55.2	1.493	.0196	28.4	1.511	.0243	23.8	1.424	.0182	-46.5
						1.521	.0283	31.2	1.403	.0188	-56.3

FIGURE 9

Dielectric dispersion at 1 Mc., 0.55 Mc., and 100 Kc. of paper containing adsorbed water at the inscribed percentages.

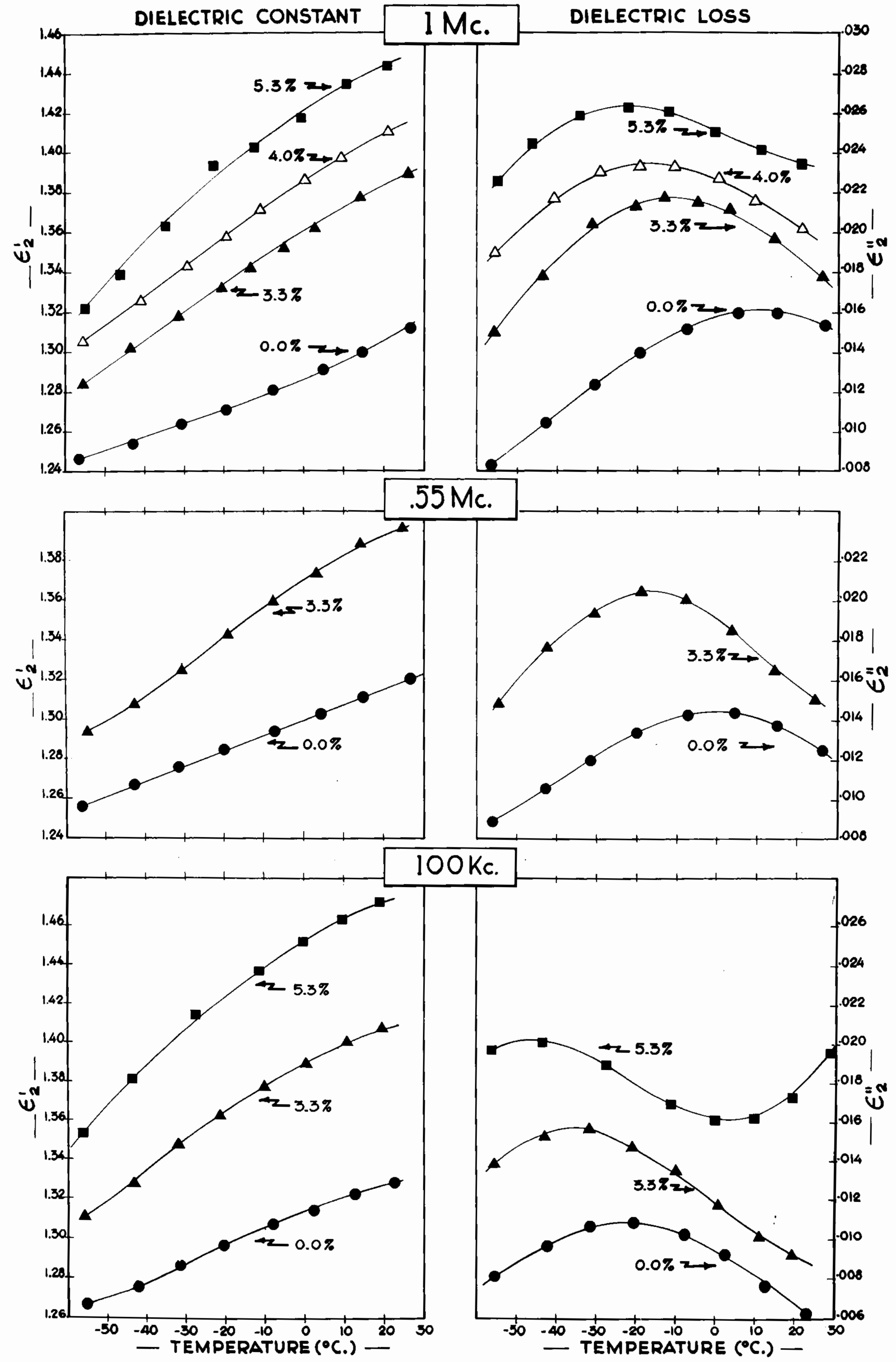
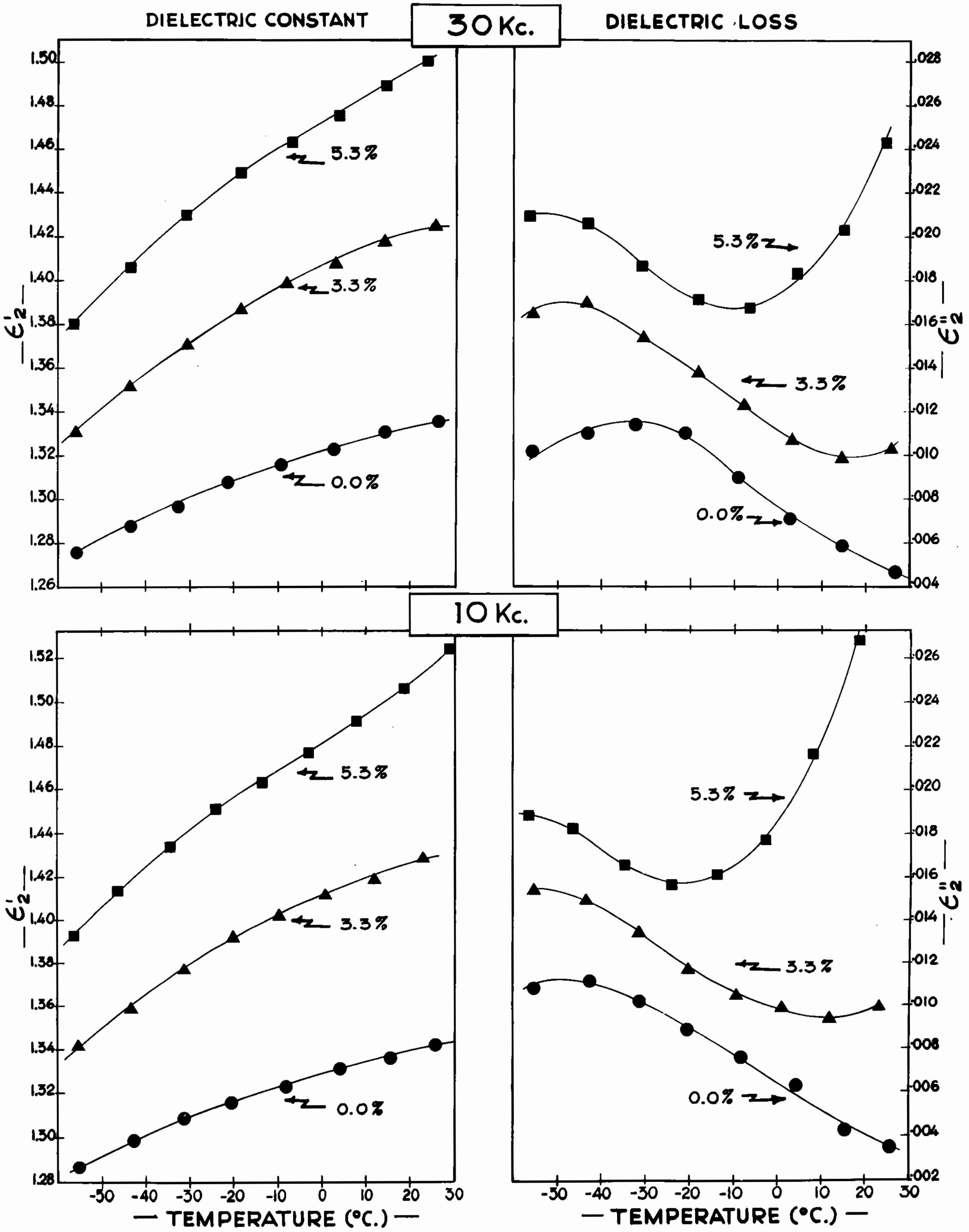

DIELECTRIC CONSTANT
1 Mc.
DIELECTRIC LOSS
.55 Mc.
100 Kc.
5.3%
4.0%
3.3%
0.0%
ϵ_2'
ϵ_2''
1.24
1.26
1.28
1.30
1.32
1.34
1.36
1.38
1.40
1.42
1.44
1.46
.006
.008
.010
.012
.014
.016
.018
.020
.022
.024
.026
.028
.030
-50
-40
-30
-20
-10
0
10
20
30
— TEMPERATURE (°C.) —

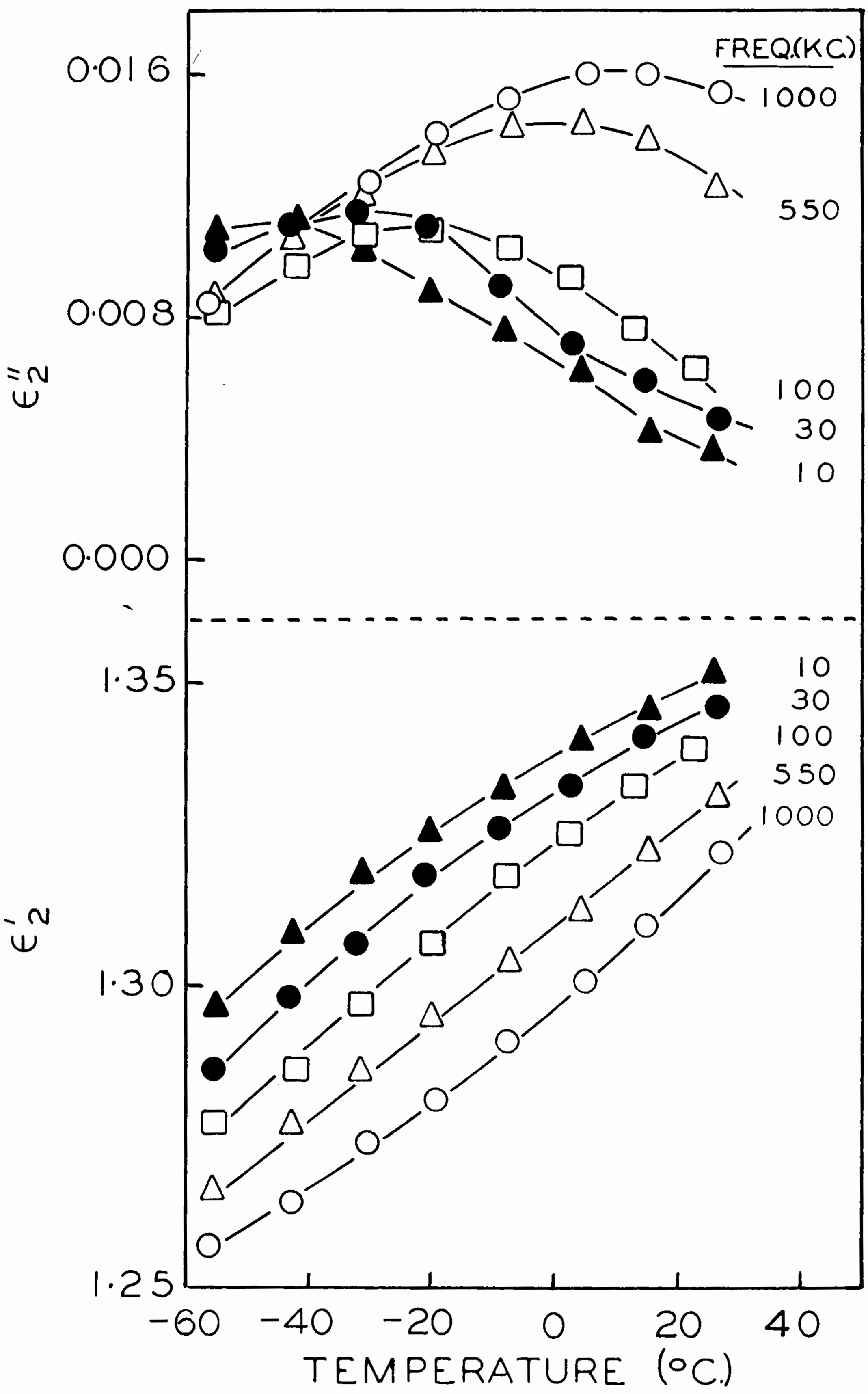
FIGURE 10

Dielectric dispersion at 30 and 10 Kc. of paper containing adsorbed water at the inscribed percentages.

FIGURE 11

Dielectric dispersion of dry paper at the inscribed frequencies.


DIELECTRIC CONSTANT
30 Kc.
DIELECTRIC LOSS
ϵ'_2
1.50
1.48
1.46
1.44
1.42
1.40
1.38
1.36
1.34
1.32
1.30
1.28
1.26
5.3%
3.3%
0.0%
ϵ''_2
.028
.026
.024
.022
.020
.018
.016
.014
.012
.010
.008
.006
.004
10 Kc.
1.52
.002
-50
-40
-30
-20
-10
0
10
20
30
— TEMPERATURE (°C.) —


FREQ.(KC.)
1000
550
100
30
10
0·016
0·008
0·000
ϵ_2''
10
30
100
550
1000
1·35
1·30
1·25
ϵ_2'
-60
-40
-20
0
20
40
TEMPERATURE (°C.)

constant.

A glance at tables of refractive index and low frequency dielectric constant show much smaller absolute differences in the former case than in the latter, especially when one is considering polar liquids like water. (The former case corresponds in general to differences in optical dielectric constant, the relationship being

$$\epsilon_{\infty} = n^2$$

where n is the refractive index.) This is because dipole orientation is involved in the measurement of ϵ_0 but not in the measurement of ϵ_{∞}. Thus, at temperatures below the dispersion region, the effect of water on the dielectric constant of cellulose will be slight because only ϵ_{∞} is involved. At temperatures above the dispersion region, on the other hand, the effect is considerably greater because one is now concerned with values of ϵ_0.

At the same time moisture causes a distinct increase in $(\epsilon''_2)_{max}$. This is presumably a result of the increase in concentration of rotating hydroxyl groups contributed by the water. A similar effect has been observed in the case of terylene (48), which, like cellulose, has hydroxyl groups responsible for dielectric dispersion at characteristic frequencies and temperatures.

Probably the most significant feature of the results is the shift of T_m toward lower temperatures by an increase in moisture content. This is shown in Table XVIII together with the corresponding variation in $(\epsilon''_2)_{max}$. The effect is similar to that produced by a lowering in the frequency of measurement. Thus, an increase in moisture content lowers the temperature at which the rotating dipoles lose their ability to follow the field, signifying a decrease in the restriction to rotation. A similar effect, observed previously in several other systems (11, 22, 52), was mentioned in the Introduction. T_m for dry paper at 1 Mc. was 10°C., compared with 16°C. determined from Stoops' data for dry cellophane at the same frequency (57). The difference may be accounted for on the basis of the residual moisture in the dry paper as defined in this work, Stoops having dried his sample by heating at 105°C.

The high temperature increase in ϵ''_2 observed at the lower frequencies and the higher moisture contents has already been mentioned in the review of the preliminary results. The additional effect of frequency observed here still does not point to its origin as either in ionic conductance or in a high temperature absorption region. This is easily seen by reasoning as follows: If the effect has its origin in high temperature absorption due to dipole orientation, then a decrease in the frequency of measurement ought to shift the absorption region to lower temperatures. Ionic conductance as well will manifest itself at lower temperatures the lower the frequency of measurement. Thus, unless the temperature (or frequency, or both) range of investigation is wide enough, it is difficult to distinguish between the two effects, as is the case in this work.

Methanol and Ethanol

Results were obtained for methanol contents of 0.0 to 7.0% at

100, 200, 550, and 1000 Kc., and are presented in Tables VIII to XIII. The effect of methanol on the dispersion region studied here was typically the same as observed for water, although there were significant differences in degree in some instances. E.g., the rate of increase of $(\epsilon''_2)_{max}$ with vapor content at a particular frequency was significantly smaller for methanol than for water. This is to be expected on the basis of the assumption that the dispersion region is due to hydroxyl groups, since there are fewer groups per gram of methanol than per gram of water. This point will be further discussed later. The same effect was observed for the rate of increase of ϵ'_2 with vapor content at a particular temperature and frequency, the rate being higher for water than for methanol. The high temperature rise in ϵ''_2 appeared at a higher vapor content in the case of methanol than in that of water. This is apparent in the loss curves at 100 Kc. for the two cases (Figures 9 and 12a). The comparative effect of the two vapors in shifting the position of the dispersion region will be discussed in a later section.

In the meantime there appears in the loss curves for methanol a characteristic break between -20 and -10°C. not observed at all in the curves for water. The effect becomes more marked at higher methanol contents; this is observed in Figure 12a showing the results at 100 Kc. There is no corresponding break in the dielectric constant curves. Furthermore, the effect appears only in the cases where the runs were performed by cooling. Thus, at 200 Kc., where the runs were performed by heating, the effect does not appear. This is likewise the case where T_m occurs in or near the temperature range of break, as in the runs at 550

FIGURE 12

a) Dielectric loss at 100 Kc. of paper containing adsorbed methanol at the inscribed percentages.

b) Dielectric constant at 100 Kc. of paper containing adsorbed methanol at the inscribed percentages.

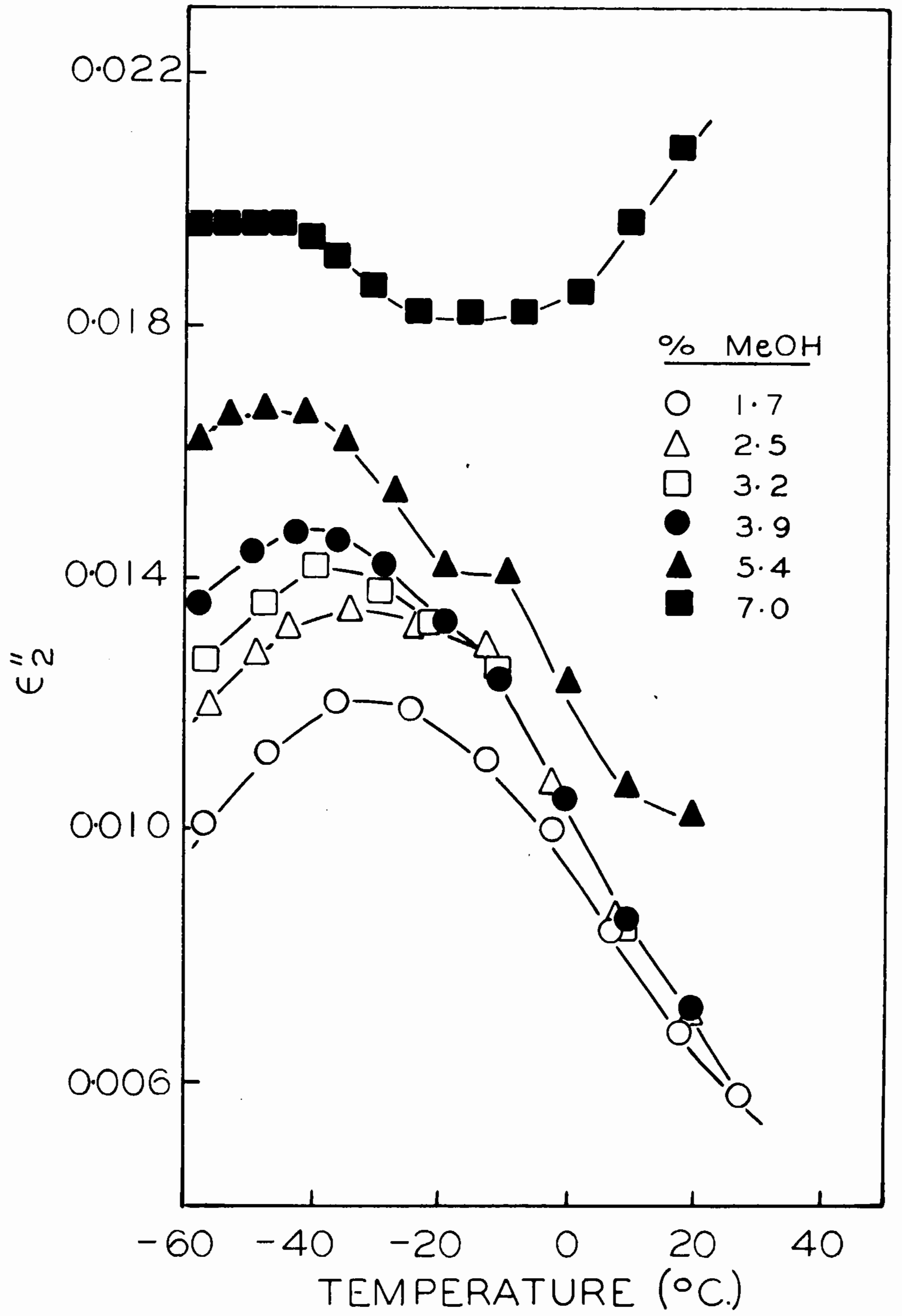

0·022
0·018
0·014
0·010
0·006
ϵ_2''
-60
-40
-20
0
20
40
TEMPERATURE (°C.)
% MeOH
○ 1·7
△ 2·5
□ 3·2
● 3·9
▲ 5·4
■ 7·0

TABLE VIII

Dielectric Dispersion of Paper containing 1.7% adsorbed methanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.272	.0110	-57.2	1.278	.0103	-56.5	1.290	.0094	-57.6	1.291	.0101	-57.2
1.280	.0129	-46.4	1.288	.0121	-45.2	1.302	.0105	-46.6	1.302	.0112	-47.3
1.288	.0147	-35.2	1.300	.0138	-33.4	1.312	.0118	-35.5	1.312	.0120	-36.3
1.300	.0164	-22.6	1.310	.0151	-21.4	1.324	.0126	-23.2	1.325	.0119	-24.5
1.310	.0178	-10.6	1.322	.0158	-8.5	1.336	.0121	-11.4	1.336	.0111	-13.0
1.322	.0185	0.7	1.334	.0152	3.2	1.346	.0111	-0.4	1.344	.0100	-2.6
1.334	.0180	13.3	1.347	.0138	15.5	1.355	.0095	9.8	1.352	.0084	7.2
1.344	.0165	24.6	1.355	.0125	25.7	1.361	.0079	19.5	1.359	.0068	17.6
						1.366	.0069	28.7	1.365	.0058	26.8

TABLE IX

Dielectric Dispersion of Paper containing 2.5% adsorbed methanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.280	.0122	-57.2	1.362	.0134	19.4	1.300	.0120	-56.3	1.372	.0071	19.3
1.288	.0144	-46.2	1.352	.0151	8.7	1.310	.0131	-46.2	1.365	.0087	8.4
1.300	.0164	-35.2	1.341	.0164	-2.0	1.321	.0142	-36.4	1.358	.0108	-2.2
1.312	.0178	-24.3	1.331	.0171	-12.6	1.333	.0144	-25.3	1.350	.0129	-12.4
1.324	.0187	-13.1	1.319	.0166	-23.3	1.344	.0139	-14.5	1.338	.0132	-23.7
1.334	.0187	-1.7	1.309	.0154	-34.6	1.355	.0132	-2.4	1.327	.0135	-34.0
1.346	.0185	8.6	1.299	.0138	-45.2	1.364	.0111	7.9	1.316	.0132	-43.7
1.353	.0173	18.5	1.288	.0116	-58.0	1.371	.0095	18.4	1.310	.0128	-49.0
1.364	.0162	28.2				1.377	.0082	27.3	1.302	.0120	-56.7

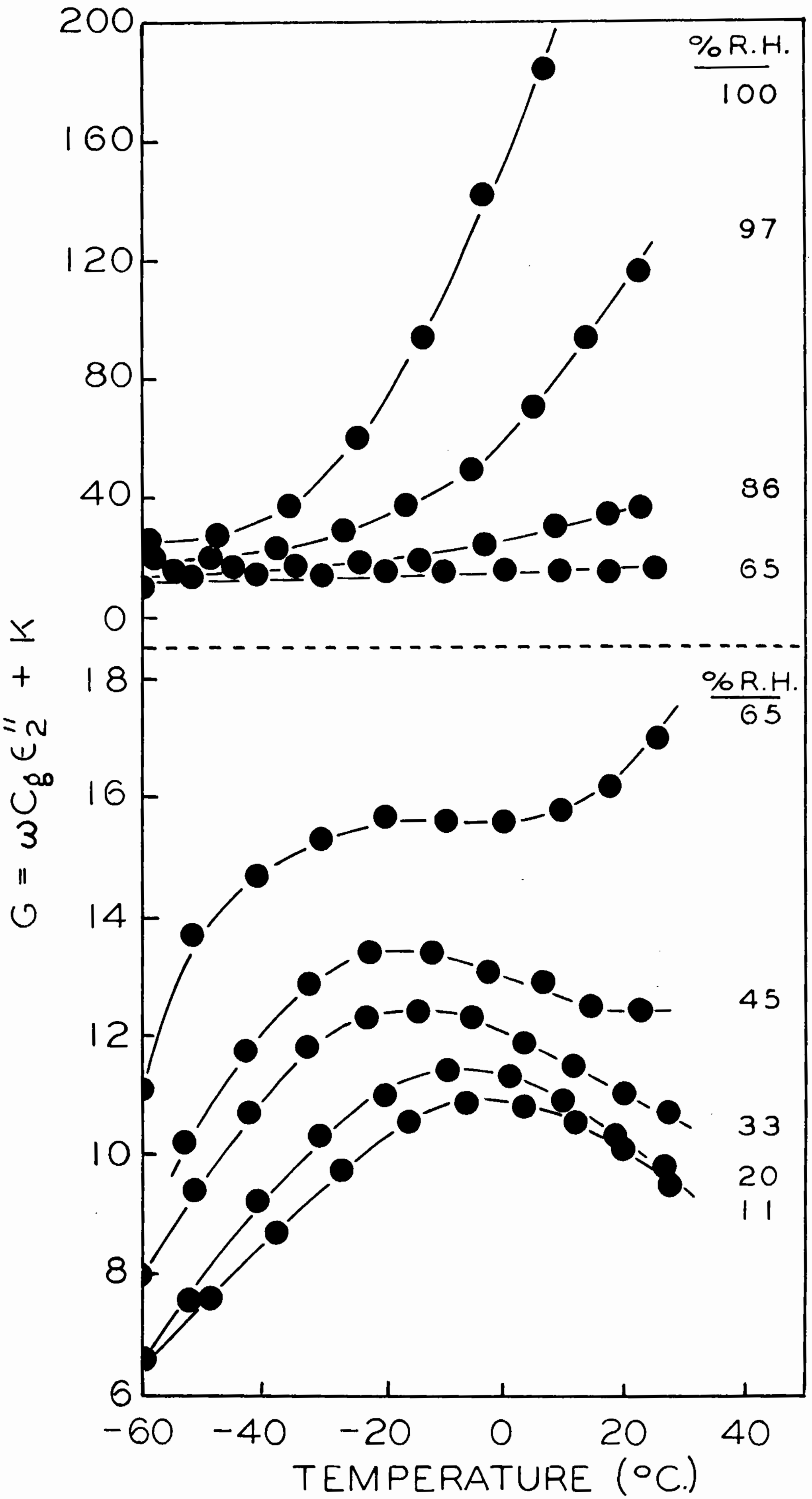

200
160
120
80
40
0
18
16
14
12
10
8
6
-60
-40
-20
0
20
40
TEMPERATURE (°C.)
G = ωC₀ε₂″ + K
% R.H.
100
97
86
65
% R.H.
65
45
33
20
11

TABLE X

Dielectric Dispersion of Paper containing 3.2% adsorbed methanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.291	.0145	-56.4	1.375	.0137	19.4	1.309	.0128	-56.7	1.384	.0071	19.5
1.300	.0166	-45.6	1.368	.0153	9.6	1.324	.0144	-44.7	1.380	.0084	9.2
1.310	.0180	-35.8	1.358	.0169	-0.6	1.336	.0150	-34.8	1.372	.0105	-1.2
1.322	.0194	-25.5	1.347	.0179	-11.3	1.347	.0150	-24.4	1.365	.0126	-11.1
1.334	.0201	-14.7	1.336	.0178	-22.2	1.358	.0140	-14.9	1.353	.0133	-21.6
1.347	.0201	-3.7	1.324	.0170	-31.6	1.368	.0129	-4.6	1.344	.0138	-29.6
1.358	.0194	6.3	1.315	.0160	-40.1	1.377	.0113	4.9	1.333	.0142	-39.5
1.368	.0183	17.2	1.306	.0146	-48.7	1.384	.0097	16.4	1.322	.0136	-47.9
1.375	.0167	26.7	1.299	.0130	-57.0	1.390	.0079	27.3	1.310	.0127	-57.3

TABLE XI

Dielectric Dispersion of Paper containing 3.9% adsorbed methanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.297	.0156	-57.0	1.386	.0144	16.7	1.319	.0136	-56.7	1.399	.0072	19.4
1.310	.0180	-43.5	1.377	.0164	6.5	1.334	.0147	-46.2	1.393	.0086	9.3
1.321	.0199	-34.4	1.368	.0178	-2.0	1.347	.0155	-36.3	1.386	.0105	-0.6
1.333	.0207	-25.2	1.359	.0186	-10.5	1.359	.0153	-26.5	1.378	.0124	-10.5
1.344	.0212	-15.8	1.350	.0190	-18.4	1.369	.0142	-17.1	1.369	.0133	-19.5
1.355	.0213	-7.1	1.343	.0188	-26.9	1.381	.0134	-6.7	1.361	.0142	-28.9
1.364	.0208	1.2	1.333	.0181	-34.8	1.388	.0115	3.5	1.352	.0146	-36.4
1.371	.0199	10.2	1.325	.0174	-42.5	1.396	.0103	12.5	1.343	.0147	-43.0
1.380	.0187	18.7	1.315	.0161	-50.3	1.399	.0087	20.5	1.334	.0144	-49.7
1.386	.0176	26.5	1.308	.0147	-58.0	1.403	.0076	28.8	1.324	.0136	-57.8

TABLE XII

Dielectric Dispersion of Paper containing 5.4% adsorbed methanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.321	.0191	-56.8	1.418	.0152	18.4	1.344	.0160	-57.3	1.430	.0103	19.5
1.328	.0204	-49.6	1.408	.0167	9.6	1.361	.0169	-46.7	1.425	.0107	9.4
1.339	.0215	-42.2	1.399	.0188	-0.2	1.372	.0169	-39.4	1.419	.0124	0.1
1.350	.0224	-33.6	1.390	.0200	-8.4	1.383	.0165	-31.2	1.414	.0141	-9.4
1.361	.0226	-26.2	1.383	.0210	-15.7	1.392	.0158	-24.3	1.403	.0142	-19.3
1.369	.0226	-19.7	1.374	.0211	-22.4	1.403	.0147	-13.8	1.394	.0154	-27.1
1.380	.0225	-11.3	1.366	.0212	-28.6	1.412	.0140	-4.2	1.384	.0162	-35.0
1.390	.0220	-3.7	1.359	.0212	-35.1	1.419	.0127	5.8	1.375	.0166	-41.4
1.399	.0213	4.7	1.352	.0207	-42.1	1.425	.0108	16.3	1.366	.0167	-47.6
1.406	.0199	14.0	1.341	.0199	-49.2	1.428	.0100	25.2	1.358	.0166	-53.4
1.412	.0183	24.4	1.330	.0188	-58.0				1.350	.0162	-58.0

TABLE XIII

Dielectric Dispersion of Paper containing 7.0% adsorbed methanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.356	.0235	-57.5	1.452	.0202	19.7	1.386	.0205	-56.6	1.475	.0208	17.7
1.368	.0246	-49.6	1.444	.0206	11.3	1.396	.0206	-51.1	1.472	.0196	9.8
1.380	.0250	-43.3	1.437	.0212	1.6	1.405	.0209	-45.4	1.466	.0185	1.7
1.388	.0255	-37.4	1.428	.0218	-6.6	1.414	.0205	-40.0	1.459	.0182	-6.8
1.400	.0258	-29.9	1.422	.0223	-13.6	1.424	.0200	-33.4	1.452	.0182	-15.2
1.411	.0254	-22.4	1.415	.0226	-20.2	1.433	.0195	-27.2	1.443	.0182	-23.3
1.421	.0248	-15.0	1.405	.0230	-27.5	1.442	.0190	-19.7	1.434	.0186	-30.5
1.430	.0246	-6.7	1.394	.0232	-34.7	1.450	.0188	-12.2	1.425	.0191	-36.6
1.440	.0238	3.5	1.387	.0232	-40.6	1.459	.0188	-2.0	1.419	.0194	-40.4
1.446	.0230	13.4	1.378	.0229	-46.2	1.465	.0188	6.6	1.412	.0196	-45.3
1.450	.0222	22.5	1.372	.0226	-51.0	1.469	.0189	16.4	1.405	.0196	-49.6
1.452	.0219	27.9	1.361	.0219	-58.3	1.474	.0196	26.6	1.399	.0196	-53.6
									1.392	.0196	-58.0

and 1000 Kc. (see Table XIX).

Results were obtained for ethanol contents of 0.0 to 8.5% at 100, 200, 550 and 1000 Kc. and are presented in Tables XIV to XVII. After completion of the runs on paper containing 8.5% ethanol, it was decided that each subsequent run should be performed over a complete temperature cycle in order to determine the existence and the nature of the effect described above for methanol. The results at 100 Kc. for paper containing 4.6% ethanol are shown in Figure 13 and are believed to represent this effect in a typical fashion. It is shown to be a hysteresis of some kind occurring over the temperature range - 20 to 20°C.; the break in the curve obtained by cooling occurs in the range -20 to -10°C. as with methanol. Also as in the case with methanol there is no corresponding irregularity in the ϵ'_2 curves. If the effect were due to some second-order phase transition, the hysteresis could be explained, although there is no reason why this should not also appear in the ϵ'_2 curves. The facts point to its occurring over the same temperature range in the case of both methanol and ethanol; this may signify some effect which both substances have on cellulose.

In other respects, the results for ethanol stood in the same relation to those for methanol as the latter did to those for water. No high temperature increase in ϵ''_2 was observed in any of the ethanol curves. The variation of T_m and $(\epsilon''_2)_{max}$ with vapor content in the three cases is shown in Tables XVIII to XX. It was found that when $(\epsilon''_2)_{max}$ was plotted against vapor content the plots were linear within experimental error; furthermore, there was a characteristic slope for each

TABLE XIV

Dielectric Dispersion of Paper containing 2.3% adsorbed ethanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.280	.0121	-57.3	1.287	.0117	-57.2	1.299	.0115	-56.4	1.302	.0120	-57.6
1.286	.0140	-49.0	1.296	.0131	-49.6	1.308	.0126	-48.6	1.310	.0131	-48.8
1.294	.0159	-40.0	1.302	.0145	-41.6	1.315	.0136	-41.2	1.319	.0138	-41.2
1.303	.0178	-30.8	1.310	.0158	-33.4	1.324	.0144	-32.8	1.330	.0139	-32.5
1.312	.0187	-22.3	1.319	.0168	-24.6	1.334	.0144	-24.0	1.340	.0135	-22.9
1.321	.0196	-13.2	1.327	.0172	-16.4	1.343	.0142	-15.3	1.347	.0126	-14.6
1.328	.0199	-4.5	1.336	.0172	-8.6	1.352	.0132	-6.6	1.355	.0118	-6.6
1.337	.0194	+3.4	1.344	.0167	0.2	1.359	.0124	1.9	1.362	.0112	1.6
1.346	.0190	12.2	1.352	.0153	10.3	1.365	.0103	11.3	1.368	.0096	10.8
1.353	.0178	21.3	1.361	.0135	20.4	1.371	.0090	20.1	1.372	.0075	19.0
1.359	.0169	26.8				1.377	.0072	28.7	1.375	.0064	25.6

TABLE XV

Dielectric Dispersion of Paper containing 4.6% adsorbed ethanol at 1000, 200 and 100 Kc.

1000 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.374	.0177	23.3	1.388	.0079	23.9	1.388	.0059	25.2
1.365	.0187	14.8	1.384	.0097	15.0	1.384	.0074	16.4
1.356	.0199	5.6	1.378	.0121	6.0	1.380	.0092	8.4
1.349	.0207	-3.4	1.371	.0142	-2.6	1.375	.0122	0.0
1.338	.0210	-12.3	1.364	.0150	-10.8	1.368	.0133	-8.7
1.330	.0208	-21.2	1.355	.0155	-19.3	1.361	.0134	-16.9
1.321	.0199	-29.3	1.346	.0158	-28.2	1.352	.0142	-25.2
1.312	.0187	-37.4	1.336	.0158	-36.7	1.343	.0150	-33.4
1.300	.0171	-46.3	1.325	.0152	-44.8	1.334	.0151	-41.3
1.290	.0146	-56.7	1.318	.0147	-50.5	1.322	.0147	-49.7
1.300	.0166	-47.6	1.310	.0134	-57.2	1.312	.0137	-57.4

TABLE XV (Cont'd.)

Dielectric Dispersion of Paper containing 4.6% adsorbed ethanol at 1000, 200 and 100 Kc.

1000 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.308	.0183	-40.6	1.322	.0152	-47.7	1.322	.0147	-51.1
1.316	.0197	-31.5	1.331	.0160	-39.7	1.333	.0153	-43.1
1.328	.0206	-22.6	1.344	.0163	-29.5	1.341	.0152	-34.7
1.337	.0213	-14.3	1.355	.0158	-21.4	1.353	.0146	-25.1
1.346	.0211	-5.2	1.364	.0153	-13.2	1.362	.0134	-16.3
1.355	.0204	4.8	1.371	.0142	-3.6	1.369	.0121	-7.6
1.364	.0195	13.3	1.378	.0134	5.4	1.375	.0114	0.6
1.372	.0178	22.6	1.384	.0115	14.7	1.383	.0106	10.3
			1.390	.0089	24.5	1.386	.0074	19.8

TABLE XVI

Dielectric Dispersion of Paper containing 6.9% adsorbed ethanol at 1000, 200 and 100 Kc.

1000 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.386	.0173	25.8	1.402	.0084	24.5	1.400	.0058	25.6
1.377	.0190	16.3	1.397	.0100	15.4	1.399	.0075	16.8
1.371	.0208	7.6	1.393	.0131	6.7	1.394	.0107	8.3
1.362	.0218	-1.2	1.386	.0150	-2.4	1.390	.0125	-0.8
1.352	.0221	-10.4	1.378	.0157	-10.8	1.383	.0136	-9.7
1.341	.0220	-18.8	1.369	.0161	-18.7	1.374	.0137	-18.8
1.333	.0215	-26.8	1.359	.0168	-26.5	1.365	.0147	-26.5
1.322	.0208	-34.5	1.350	.0171	-34.5	1.356	.0156	-34.6
1.315	.0199	-42.3	1.340	.0166	-42.4	1.346	.0160	-43.3
1.306	.0180	-50.4	1.328	.0163	-50.0	1.336	.0159	-49.7

TABLE XVI (Cont'd.)

Dielectric Dispersion of Paper containing 6.9% adsorbed ethanol at 1000, 200 and 100 Kc.

1000 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.297	.0164	-57.8	1.318	.0149	-58.2	1.325	.0151	-57.5
1.306	.0178	-50.7	1.331	.0165	-50.1	1.336	.0159	-50.0
1.315	.0194	-43.6	1.340	.0171	-43.0	1.343	.0161	-43.8
1.325	.0208	-34.5	1.352	.0174	-34.7	1.353	.0162	-36.6
1.337	.0218	-25.2	1.362	.0169	-25.7	1.364	.0154	-28.1
1.347	.0225	-15.7	1.374	.0164	-17.5	1.374	.0143	-19.7
1.359	.0222	-5.7	1.383	.0152	-7.4	1.383	.0130	-10.2
1.371	.0214	4.5	1.392	.0144	2.3	1.388	.0121	-1.7
1.380	.0199	15.2	1.397	.0129	11.5	1.394	.0122	5.8
1.387	.0176	26.2	1.402	.0195	22.5	1.399	.0113	15.5
						1.402	.0074	24.6

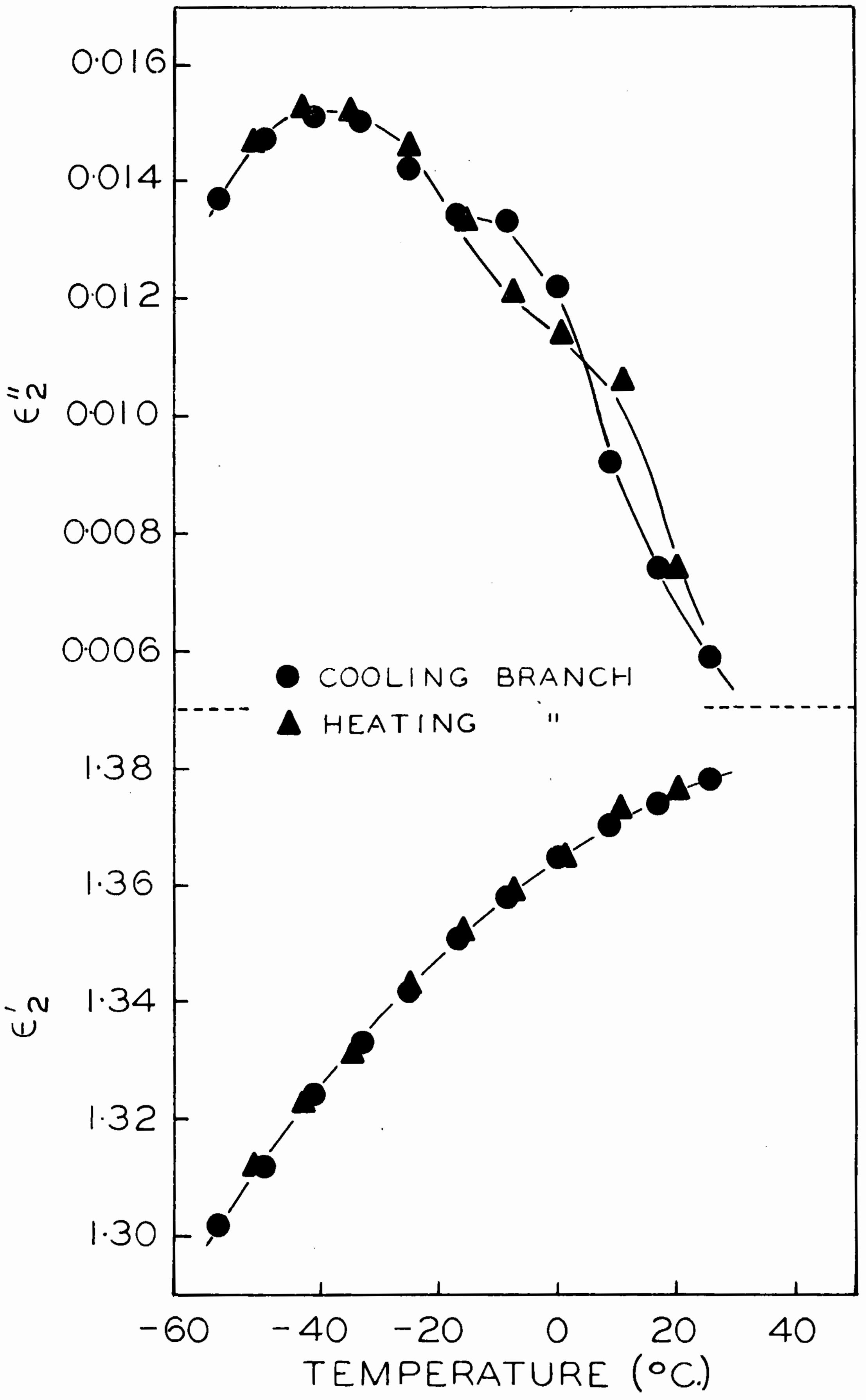
TABLE XVII

Dielectric Dispersion of Paper containing 8.5% adsorbed ethanol at 1000, 550, 200 and 100 Kc.

1000 Kc.			550 Kc.			200 Kc.			100 Kc.		
ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.	ϵ'_2	ϵ''_2	Temp.
1.409	.0183	20.8	1.415	.0133	24.3	1.340	.0163	-56.8	1.424	.0074	23.9
1.400	.0197	12.4	1.409	.0151	15.6	1.353	.0176	-49.0	1.421	.0082	15.8
1.394	.0211	3.9	1.402	.0170	7.3	1.364	.0179	-41.8	1.418	.0091	7.5
1.386	.0222	-4.7	1.394	.0187	-1.2	1.375	.0177	-33.6	1.414	.0109	-0.5
1.377	.0230	-12.8	1.387	.0204	-10.0	1.387	.0168	-25.0	1.408	.0130	-8.5
1.366	.0230	-20.5	1.377	.0210	-18.3	1.397	.0155	-16.4	1.400	.0146	-17.2
1.356	.0228	-29.4	1.366	.0214	-26.3	1.406	.0145	-8.2	1.390	.0153	-25.3
1.344	.0220	-37.7	1.356	.0214	-33.7	1.414	.0129	0.8	1.380	.0164	-33.5
1.334	.0205	-46.7	1.344	.0209	-41.6	1.419	.0108	10.5	1.369	.0168	-41.3
1.321	.0185	-56.3	1.334	.0197	-49.5	1.424	.0095	19.8	1.358	.0169	-49.8
			1.324	.0183	-56.8	1.425	.0084	26.6	1.346	.0165	-57.7

FIGURE 13

Dielectric dispersion at 100 Kc. of paper containing 4.6% adsorbed ethanol.

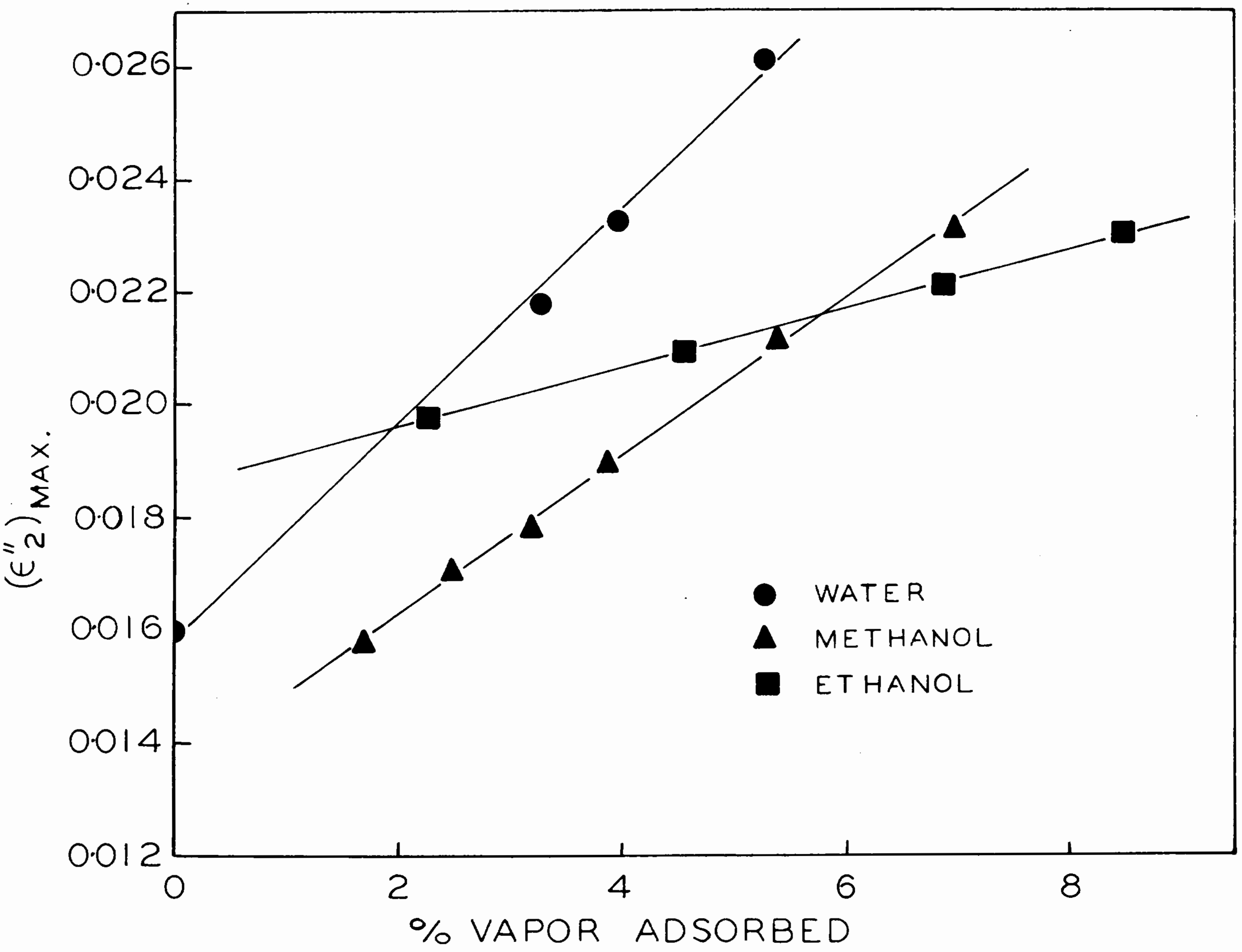

0·016
0·014
0·012
0·010
0·008
0·006
ϵ_2''
1·38
1·36
1·34
1·32
1·30
ϵ_2'
● COOLING BRANCH
▲ HEATING "
−60
−40
−20
0
20
40
TEMPERATURE (°C.)

vapor, the same value being obtained at each of the frequencies used. The best lines in each case are shown in Figure 14. The slope of each line signifies the increase in loss due to one gram of added vapor. Expression of this increase in terms of added hydroxyl groups ought to be a good test of the assumption that the dispersion region here studied is due to these groups. In Table XXIa the increase in loss due to one gram of hydroxyl is shown for each case. The agreement is surprising when one considers that the logical basis for comparison should be the area under the ϵ''_2 curves rather than $(\epsilon''_2)_{max}$, since in all probability a distribution of relaxation times is involved. Extension of the temperature range of investigation here employed ought to make such comparison possible.

This is more readily seen by considering similar calculations made for terylene, a polyester which, like cellulose, is characterized by a dispersion region attributable to hydroxyl groups (48). Terylene is normally 40% crystalline, but can be obtained as a completely amorphous material. Dielectric data were obtained for both forms in the dry as well as in the wet state. The evidence shows that water is absorbed by the amorphous polymer, or into the amorphous regions of the partially crystalline material, as in the case of cellulose. Also, it is only in the amorphous regions that the dielectric process operates which is responsible for the losses. Although these losses are different for the two forms, one would expect the loss per gram of added water (or per hydroxyl group) to be the same. Equivalent expressions for this parameter are presented in Table XXIb. Calculation directly from ϵ''_{max} gives

FIGURE 14

Effect of vapor content on $(\epsilon''_2)_{max}$.


0·026
0·024
0·022
0·020
0·018
0·016
0·014
0·012
$(\epsilon''_2)_{MAX.}$
0
2
4
6
8
% VAPOR ADSORBED
● WATER
▲ METHANOL
■ ETHANOL

results deviating from the average by 5.8% while the deviation obtained by using as criterion the area under the ϵ'' curve is only 3%.

Sillars, as quoted by Reddish (48), found that the area under ϵ''-ln f curves is in the same relation to the number of dipoles and their moment whatever the distribution of relaxation times. In an ideal case where a single relaxation time is involved this area is $\pi\epsilon''_{max}$ so that ϵ''_{max} can be regarded as a direct measure of the number of dipoles. However, when there is a spread of relaxation times, this is no longer the case, and one must then resort to measurement of areas.

It must be kept in mind that in Table XXIa the loss is expressed in terms of the compound dielectric cellulose-vapor -- vapor, as defined in the Analysis of Dielectric, while in Table XXIb the loss is a direct property of terylene. Comparison of the measurements for the two polymers is therefore difficult under these conditions, but can be attempted in an approximate manner as shown in the Discussion.

TABLE XVIII

Variation of T_m and $(\epsilon''_2)_{max}$ with amount of water adsorbed.

Frequency (Kc.)	Rel. vap. press.	Water adsorbed: per cent of dry weight	ϵ''_{max}	T_m(°C)
1000	0.0	0.0	.0160	10
	22.3	3.3	.0218	-12
	32.4	4.0	.0233	-17
	46.6	5.3	.0262	-21
550	0.0	0.0	.0144	0
	22.3	3.3	.0205	-17
	46.6	5.3	-	-
100	0.0	0.0	.0109	-24
	22.3	3.3	.0157	-35
	46.6	5.3	.0201	-47
30	0.0	0.0	.0114	-36
	22.3	3.3	.0169	-48
	46.6	5.3	-	-
10	0.0	0.0	.0111	-48
	22.3	3.3	-	-
	46.6	5.3	-	-

TABLE XIX

Variation of T_m and $(\epsilon''_2)_{max}$ with amount of methanol adsorbed

Frequency (Kc.)	Rel. vap. press.	Methanol sorbed; per cent of dry weight	$(\epsilon''_2)_{max}$	T_m(°C.)
1000	0.0	1.7	.0185	0
	9.6	2.5	.0187	-7
	19.3	3.2	.0201	-10
	32.1	3.9	.0213	-13
	57.1	5.4	.0226	-21
	75.5	7.0	.0258	-28
550	0.0	1.7	.0158	-8
	9.6	2.5	.0171	-15
	19.3	3.2	.0179	-16
	32.1	3.9	.0190	-19
	57.1	5.4	.0212	-26
	75.5	7.0	.0232	-35
200	0.0	1.7	.0126	-20
	9.6	2.5	.0144	-27
	19.3	3.2	.0150	-31
	32.1	3.9	.0155	-32
	57.1	5.4	.0169	-41
	75.5	7.0	.0209	-47
100	0.0	1.7	.0120	-30
	9.6	2.5	.0135	-34
	19.3	3.2	.0142	-37
	32.1	3.9	.0147	-41
	57.1	5.4	.0167	-47
	75.5	7.0	-	-

TABLE XX

Variation of T_m and $(\epsilon''_2)_{max}$ with amount of ethanol adsorbed

Frequency (Kc.)	Rel. vap. press.	Ethanol sorbed: per cent of dry weight	$(\epsilon''_2)_{max}$	T_m(°C.)
1000	0.0	2.3	.0198	-5
	23.7	4.6	.0210	-12
	40.0	6.9	.0222	-13
	65.1	8.5	.0231	-21
550	0.0	2.3	.0172	-13
	23.7	4.6	-	-
	40.0	6.9	-	-
	65.1	8.5	.0214	-30
200	0.0	2.3	.0144	-25
	23.7	4.6	.0160	-32
	40.0	6.9	.0172	-35
	65.1	8.5	.0179	-40
100	0.0	2.3	.0140	-33
	23.7	4.6	.0151	-39
	40.0	6.9	.0161	-44
	65.1	8.5	.0170	-47

TABLE XXIa

Increase in $(\epsilon''_2)_{max}$ for cellulose due to the hydroxyl groups of the adsorbed vapor.

Vapor adsorbed	Loss per g. vapor	Dev^n from avg. (%)	Molecular wt. of vapor	Loss per g. OH	Dev^n from avg. (%)
Water	.00188	48	18	.0020	0
Methanol	.00140	10	32	.0026	30
Ethanol	.00052	59	4b	.0014	30

TABLE XXIb

Increase in losses for terylene due to adsorbed water vapor

Material	% Adsorbed water	ϵ''_{max} at 0°C.	Area under ϵ'' - lnf curve at 0°C.	Change in ϵ''_{max} per gm. added H_2O	% dev^n from avg.	Change in area per gm. added H_2O	% dev^n from avg.
Crystalline	0.00	0.041	0.418	.0409	5.8	.418	3.0
Crystalline	0.44	0.059	0.602				
Amorphous	0.00	0.067	0.706	.0460		.394	
Amorphous	0.64	0.096	0.958				

Source of data (48)

DISCUSSION OF RESULTS

A series of experiments was performed over a frequency range of 30 to 1000 Kc. and temperature range of -58 to 26°C. The dielectric was a compound one consisting of a paper made of pure cellulose containing varying amounts of adsorbed vapor, and the vapor itself at varying pressure. A dispersion region was found for dry paper corresponding to that previously discovered for dry cellophane, a regenerated form of cellulose. It was found as well that adsorbed water, methanol and ethanol cause this dispersion region to be shifted in a systematic way.

Analysis of Dielectric

The arrangement in the experimental condenser was that of layers of paper alternating with layers of vapor, the layers being parallel to one another and to the electrodes. If a cross-section of the cell is taken perpendicular to the layers, the arrangement is a spiral one as shown in Figure 15a.

The dielectric constant and loss of this compound dielectric are referred to as ϵ'_2 and ϵ''_2, respectively. Following is a method of calculating from these measured values the corresponding ones ϵ'_1 and ϵ''_1 for the paper itself, and finally, ϵ' for pure native cellulose.

For the calculation of ϵ'_1 and ϵ''_1 a model was chosen of n layers of paper alternating with (n + 1) layers of vapor, as shown in Figure 15b. C_1 is the capacitance of the vapor layer (assumed to be a pure capacitance), while C_2 and G_2 are the parallel capacitance and conductance for a single layer of paper. C_p and G_p represent the measured capacitance and conductance. It is assumed that $G^2_2 \ll \omega^2 C^2_2$, so that all powers of G_2 higher than the square can be neglected. An equivalent condition is that $(\epsilon''_1)^2 \ll (\epsilon'_1)^2$. This is true to within less than 0.1% for the data of Table XXII, and consequently for the major part of this work.

The admittance of the model, Y, can be shown to be given by:

$$Y^2 = \omega^2 C_2^2 \frac{C_1^2}{\left[nC_1 + (n+1)C_2\right]^2} + G_2^2 \frac{nC_1^3}{\left[nC_1 + (n+1)C_2\right]^3}$$

Whence:

$$C_p = C_2 \left[\frac{C_1}{nC_1 + (n+1)C_2}\right]$$

$$G_p = G_2 \left[\frac{nC_1^3}{\left(nC_1 + (n+1)C_2\right)^3}\right]^{\frac{1}{2}}$$

These equations are expressed in terms of dielectric constants and losses, thus:

$$\epsilon'_2 = \epsilon'_1 \left[\frac{1}{V_2/V + \epsilon'_1 V_1/V}\right] \qquad (1)$$

$$\epsilon''_2 = \epsilon''_1 \left(\frac{V_2}{V}\right)^{\frac{1}{2}} \left[\frac{1}{V_2/V + \epsilon'_1 V_1/V}\right]^{3/2} \qquad (2)$$

Combining (1) and (2),

$$\epsilon''_2 = \epsilon''_1 \left(\frac{V_2}{V}\right)^{\frac{1}{2}} \left(\frac{\epsilon'_2}{\epsilon'_1}\right)^{3/2} \qquad (3)$$

FIGURE 15

Model for dielectric.

a) Actual arrangement.

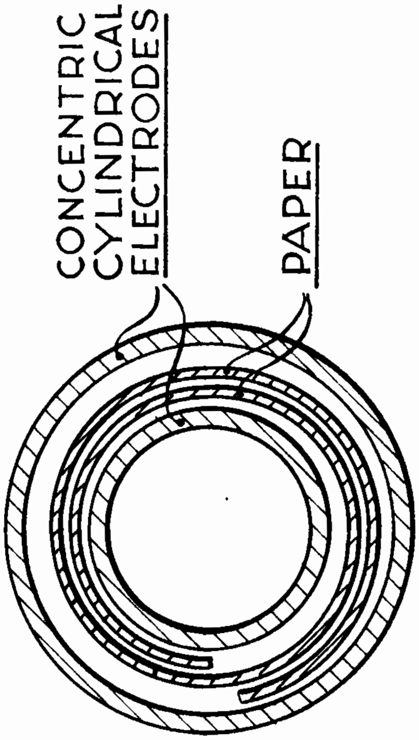
b) Theoretical model.

V_2/V represents the volume fraction of paper in the cell and $V_1/V =$ $1 - V_2/V$. Equation (1) is the same as that obtained by Argue and Maass for a similar model (2).

In Table XXII are given values of ϵ'_1 and ϵ''_1 calculated from the experimentsl results at 1 Mc. for paper containing 0 and 5.3 percent adsorbed water. The loss data are plotted in Figure 16. It is apparent that the position of the absorption region is affected very little by the transformation of the properties of the compound dielectric to those of the paper itself. In the case of the results for 5.3% water, the value of V_2/V was determined as 0.635, on the assumption that the volumes of cellulose and water are additive (4), and further assuming that the changes in volume of the fibres were duplicated in similar changes for the paper. All subsequent values of V_2/V reported were calculated on the basis of this assumption. Because of the low coefficients of thermal expansion of cellulose (19), V_2/V varied over the temperature range covered by only about 0.2%, which is well within the experimental error.

All values of ϵ'_2 reported up to now were calculated on the basis of $C_o = 9.7\ \mu\mu f.$ (see EXPERIMENTAL, Dielectric cell). Actually, this was valid only for paper sample #1, while for samples #2 and #3 the true value was $9.0\ \mu\mu f.$ Correction for this change in C_o involves a simple addition of 0.010 to the reported values of ϵ'_2, while ϵ''_2 is not affected at all. All tabulated values as well as all subsequent graphical values of ϵ'_2 are corrected for in this way.

Delevanti and Hansen (16) showed that the relationship between


CONCENTRIC CYLINDRICAL ELECTRODES
PAPER

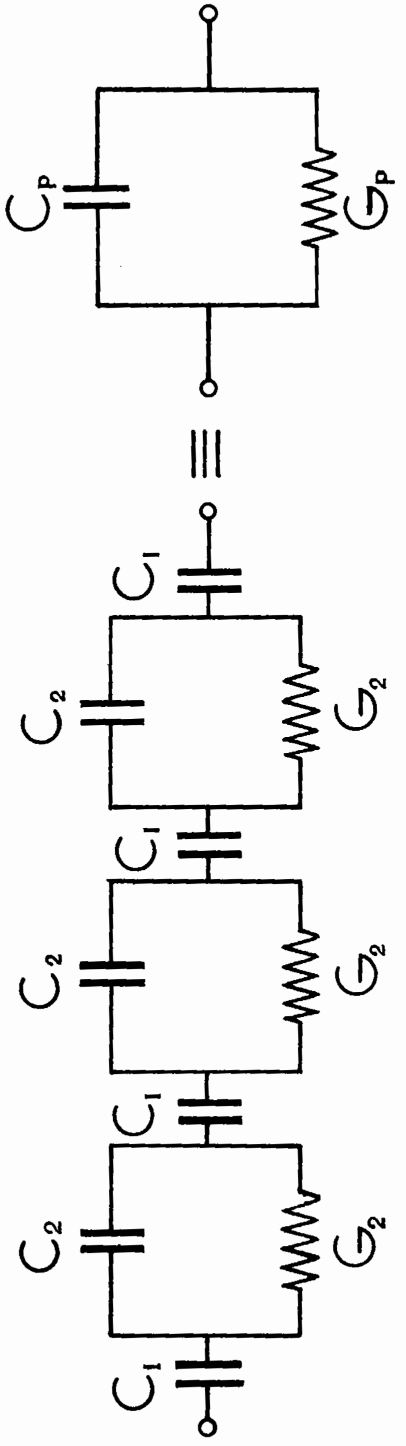

C1
C2
G2
C1
C2
G2
C1
C2
G2
C1
≡
Cp
Gp

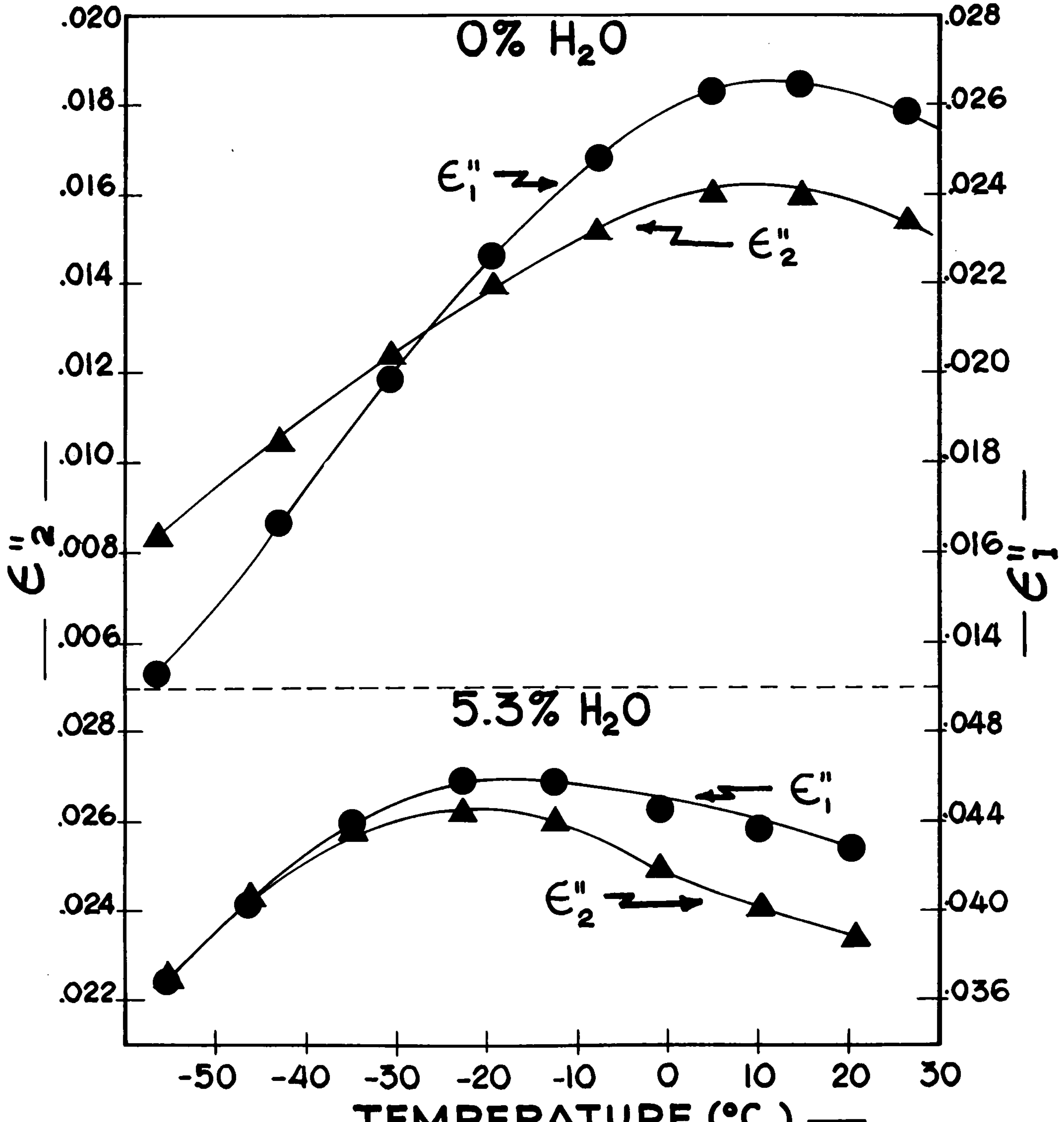
TABLE XXII

Dielectric dispersion at 1 Mc. of paper containing 0.0 and 5.3% adsorbed water

0.0% Water					5.3% Water				
Temp.	ϵ'_2	ϵ'_1	ϵ''_2	ϵ''_1	Temp.	ϵ'_2	ϵ'_1	ϵ''_2	ϵ''_1
26.5	1.322	1.638	.0154	.0268	20.4	1.453	1.964	.0234	.0462
14.6	1.310	1.610	.0160	.0276	10.2	1.444	1.939	.0241	.0471
4.8	1.301	1.587	.0160	.0273	-1.0	1.427	1.891	.0250	.0479
-7.7	1.291	1.563	.0152	.0256	-12.6	1.412	1.850	.0260	.0490
-19.4	1.281	1.540	.0140	.0234	-22.6	1.403	1.826	.0262	.0488
-30.6	1.274	1.525	.0124	.0205	-34.8	1.373	1.748	.0258	.0465
-42.9	1.264	1.502	.0105	.0172	-46.4	1.349	1.688	.0243	.0427
-56.5	1.257	1.486	.0084	.0137	-55.2	1.332	1.646	.0225	.0388

FIGURE 16

Effect of the transformation of ϵ''_2 to ϵ''_1 on dielectric dispersion at 1 Mc. of paper containing 0.0 and 5.3% adsorbed water.


0% H₂O
5.3% H₂O
ε₁''
ε₂''
ε₁''
ε₂''
.020
.018
.016
.014
.012
.010
.008
.006
.028
.026
.024
.022
.028
.026
.024
.022
.020
.018
.016
.014
.048
.044
.040
.036
-50
-40
-30
-20
-10
0
10
20
30
TEMPERATURE (°C.)
ε₂''
ε₁''

the density and dielectric constant of paper is expressed by a Clausius-Mosotti type of equation:

$$\frac{1}{d}\,\frac{\epsilon'-1}{\epsilon'+2} = K \qquad (4)$$

where d is the density and K is a constant for a particular fibre. These results were confirmed by Calkins with an improved apparatus (8).

Thus, by means of equations (1) and (4) it is possible to calculate absolute values of the dielectric constant for cellulose from values obtained for the compound dielectric paper-vapor. In Table XXIII is presented for dry cellulose at 25°C. a comparison of the results of Brown (7), Calkins (8), and the present author. Brown measured ϵ'_2 for an experimental arrangement similar to the one used in this work. His value for V_2/V was 0.648. From this and using equation (1), ϵ'_1 was calculated, this corresponding to the measured sample density of 0.610. Using equation (4) ϵ' was obtained for the cellulose fibre, assuming a density of 1.55 (33). Also, ϵ'_2 was calculated for $V_2/V = 0.625$ and a sample density of 0.496, corresponding to the arrangement in this work. Calkins measured ϵ'_1 directly; ϵ'_2 and ϵ' were obtained as described above, ϵ'_2 corresponding to the arrangement in this work.

If it is assumed that the fibres in the samples examined were in a plane perpendicular to the electrical field then the differences in the results of the various workers may be accounted for at least partially on the basis of the dielectric anisotropy of cellulose. The transverse and axial dielectric constants of the cellulose crystallite have been

TABLE XXIII

Dielectric constant of dry cellulose at 25°C.

Data	Material	Freq. (Kc.)	Reported Values		Recalculated Values	
			Density (V_2/V = .648)	Diel. Const.	ϵ'_2 Density = .496 V_2/V = .625	ϵ'
Brown	linen paper	300	.610	ϵ'_2 = 1.363	1.282	3.76
Calkins	cotton paper	1	.8	ϵ'_1 = 2.42	1.364	5.94
Present	paper of 75% linen + 25% cotton	300	($\frac{V_2}{V}$ = .625)	ϵ'_2 = 1.334★	1.334	4.96
		10	.496	1.351	1.351	5.48
		1		1.357★	1.357	5.67

★ Estimated from the results at other frequencies found to be 5.27 and 7.19, respectively, at a frequency of 300 Kc.(7). In cotton the fibrils are arranged spirally about the fibre axis whereas in linen they are nearly parallel to the fibre axis. Thus, when dielectric constants are measured transverse to the fibre axis, the values should increase in the order linen, linen + cotton, and cotton: the results given in Table XXIII fall into this order.

Using the same method, it is possible to obtain the dielectric constant of cellulose as a function of vapor content. Calculations were made from data at 1 Mc. and 20°C., and the results are shown in Table XXIV. The variation of fibre density with water content was obtained from Hermans (33). It was assumed that methanol and ethanol had no effect on fibre density. If the data on water are any criterion, there being little change over the range studied, this assumption appears quite logical.

The values of ϵ' are plotted versus vapor content in Figure 17. The rate of increase of ϵ' increases in the order ethanol, methanol, and water, the changes in the case of ethanol being very small. E.g., at 5.3% vapor content, ethanol has produced a percentage change in ϵ' of only 18, while the corresponding change in the case of water is as high as 100%. The values of ϵ' for dry paper in the curves for water, and for methanol and ethanol correspond to the values for paper samples #2 and #3. The percentage difference is only 2, which is a good check on the reproducibility of the results.

FIGURE 17

Dielectric constant of cellulose at 1 Mc. and 20°C.: its variation with amount of vapor adsorbed.

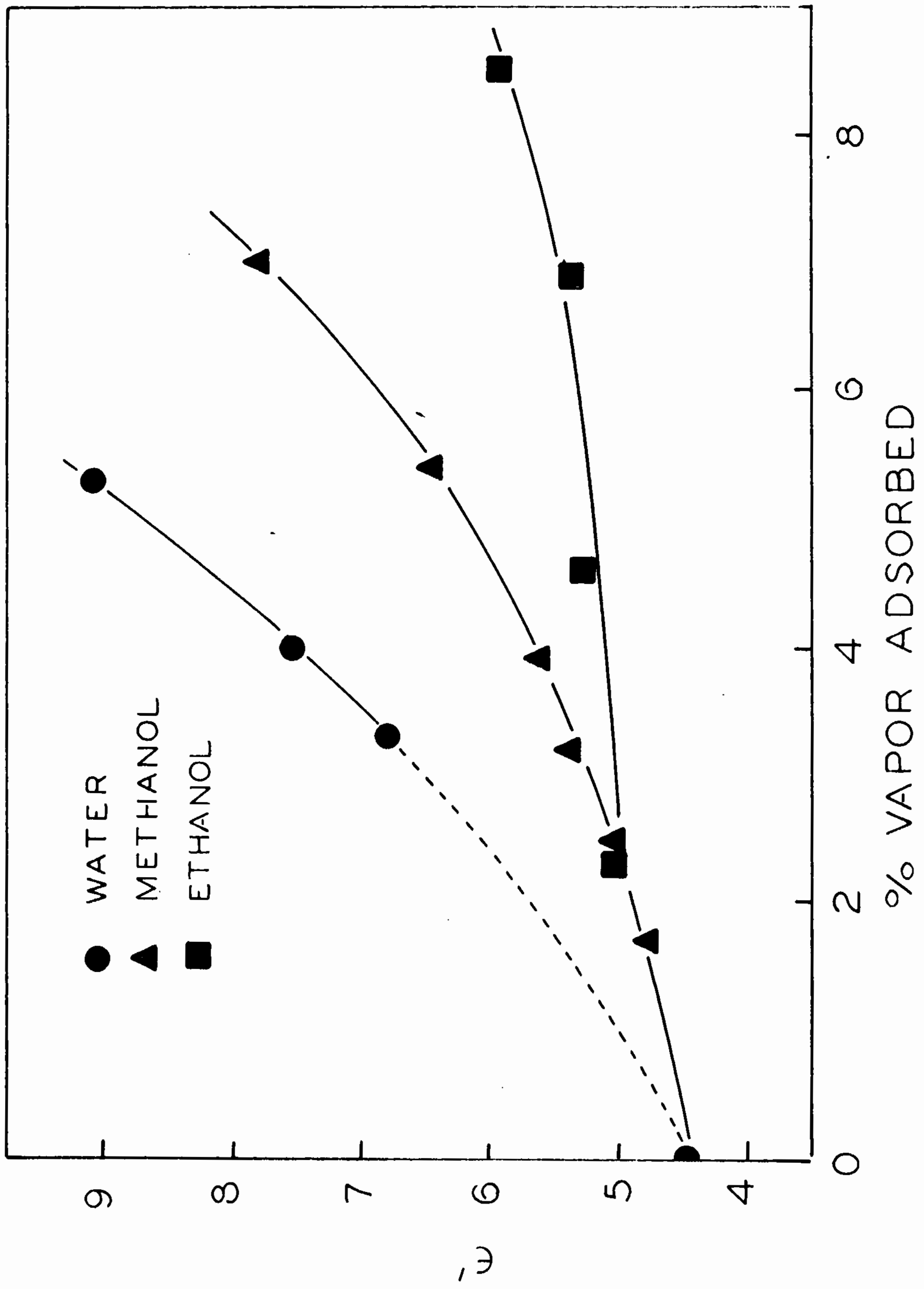

● WATER
▲ METHANOL
■ ETHANOL
ε'
4
5
6
7
8
9
0
2
4
6
8
% VAPOR ADSORBED

TABLE XXIV

Dielectric constant of cellulose at 1 Mc. and 20°C.:

its variation with amount of vapor adsorbed

% Water	V_2/V	sample density	fibre density	ϵ'_2	ϵ'_1	ϵ'
0.0	.625	.496	1.55	1.315	1.621	4.46
3.3	.630	.509	1.56	1.397	1.822	6.80
4.0	.632	.510	1.55	1.418	1.874	7.54
5.3	.635	.514	1.54	1.453	1.965	9.08
% Methanol						
1.7	.638	.503	1.55	1.341	1.663	4.78
2.5	.640	.505		1.354	1.690	5.04
3.2	.640	.508		1.368	1.725	5.39
3.9	.643	.510		1.380	1.749	5.64
5.4	.646	.515		1.410	1.819	6.46
7.0	.648	.521		1.448	1.914	7.83
% Ethanol						
2.3	.640	.504	1.55	1.353	1.688	5.04
4.6	.646	.511		1.371	1.721	5.28
6.9	.648	.520		1.382	1.744	5.36
8.5	.651	.526		1.408	1.802	5.93

Application of the Theory of Absolute Reaction Rates

In all cases in this work the linearity of the plot of log τ versus 1/T permitted analysis of the data in terms of the theory of absolute reaction rates (25, 28). As shown in the Introduction a free energy of activation for relaxation is defined:

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\Delta F^{*}/RT}$$

or, breaking up the free energy term into the entropy and enthalpy of activation,

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\Delta H^{*}/RT} e^{\Delta S^{*}/R}$$

k and h are the Boltzmann and Planck constants, respectively, and T is the absolute temperature. All values of ΔF^{*}, ΔH^{*}, and ΔS^{*} reported here are for the temperature 298°K. and were calculated as follows:

$$\Delta F^{*} = 1364 \left[12.793 + \log \tau \right]$$

$$\Delta H^{*} = 4.576\,\sigma - 592$$

$$\Delta S^{*} = \frac{1}{298} \left[\Delta H^{*} - \Delta F^{*} \right]$$

$$\sigma = \frac{\Delta(\log \tau)}{\Delta(1/T)}$$

The plots of log τ versus 1/T for paper containing adsorbed water, methanol, and ethanol, respectively, are presented in Figures 18, 19 and 20. From these plots τ was determined in each case at 298°K.

FIGURE 18

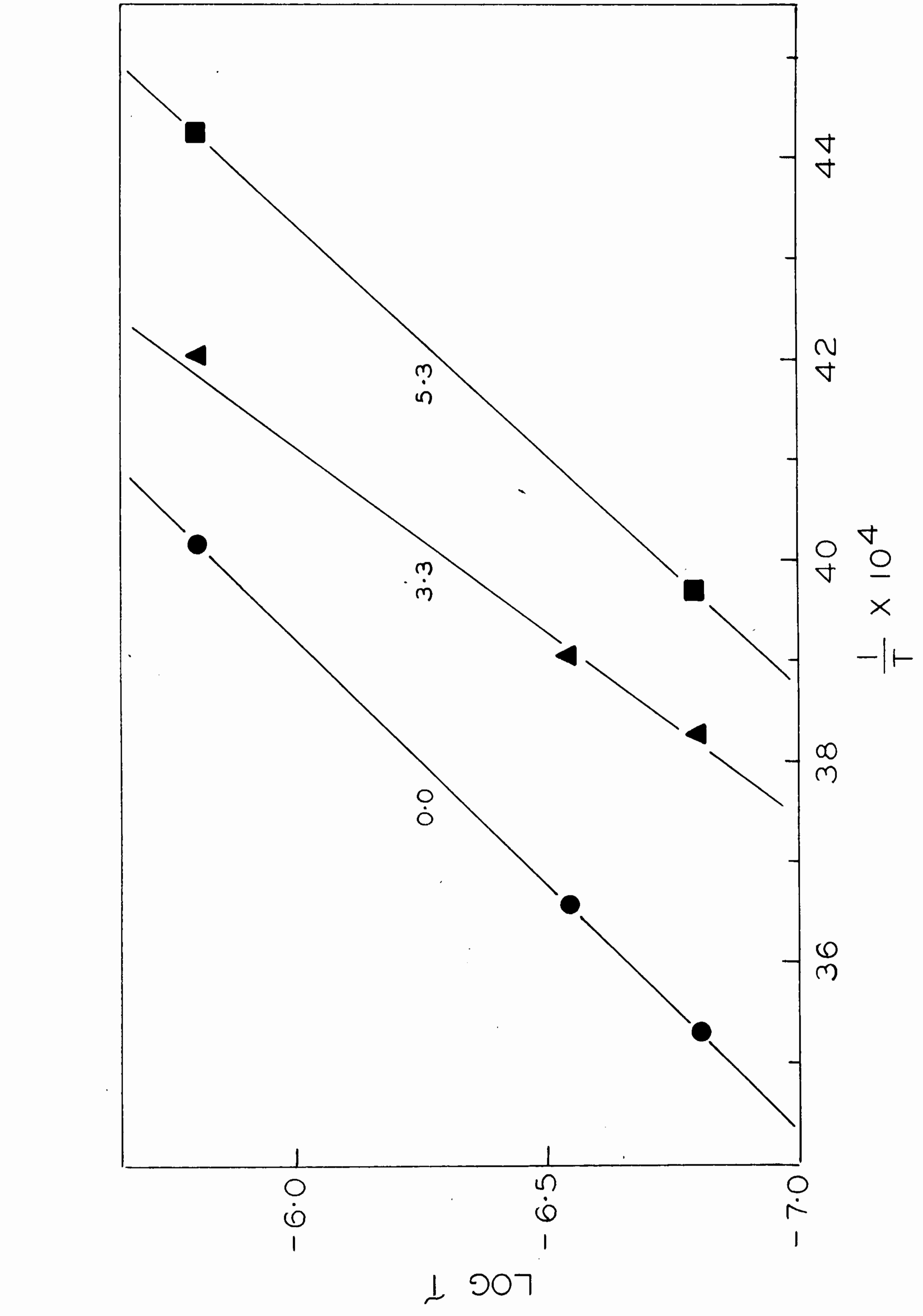
Log τ versus 1/T for paper containing 0.0, 3.3, and 5.3% adsorbed water.

FIGURE 19

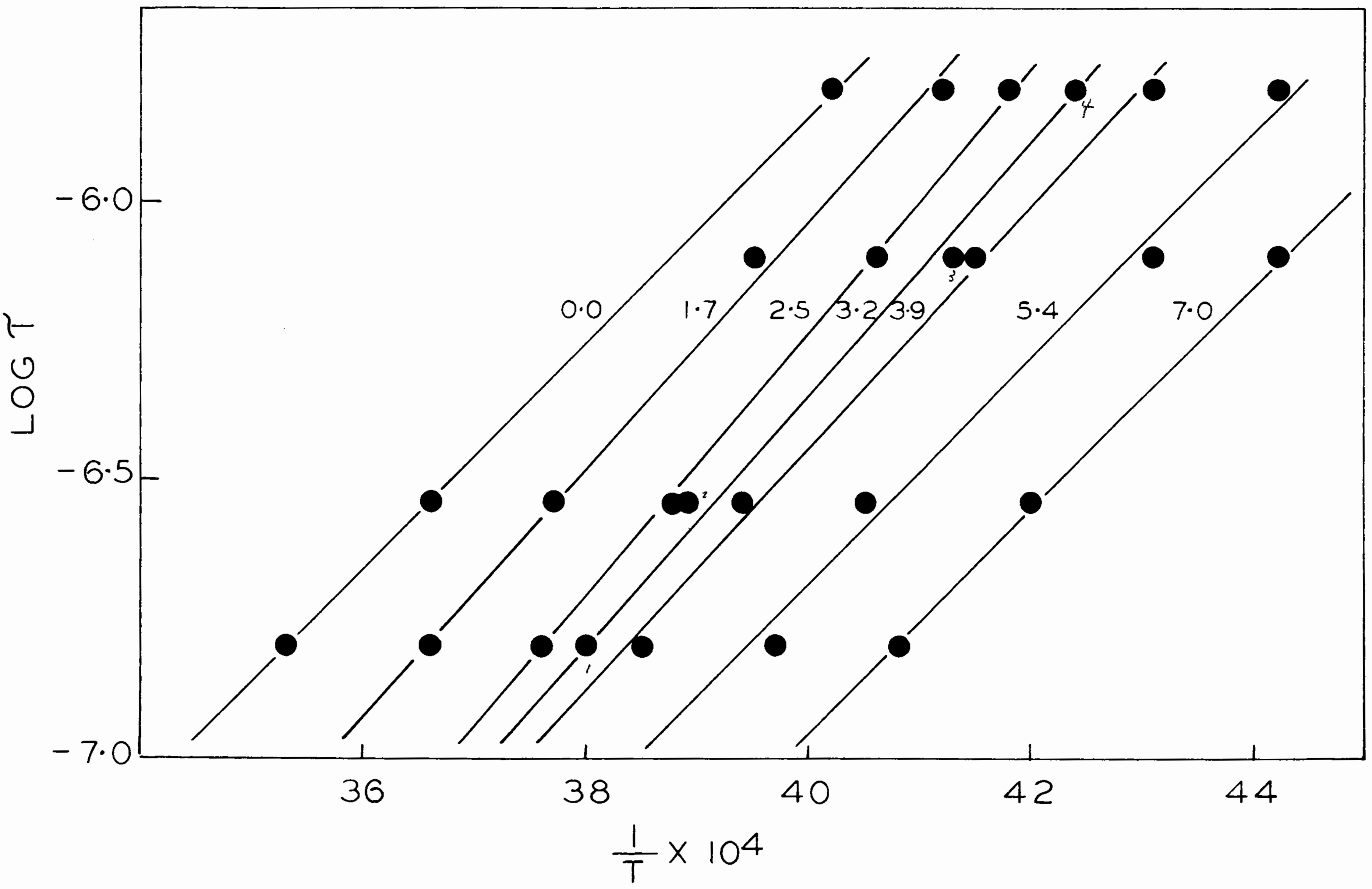
Log τ versus 1/T for paper containing 0.0, 1.7, 2.5, 3.2, 3.9, 5.4, and 7.0% adsorbed methanol.

FIGURE 20

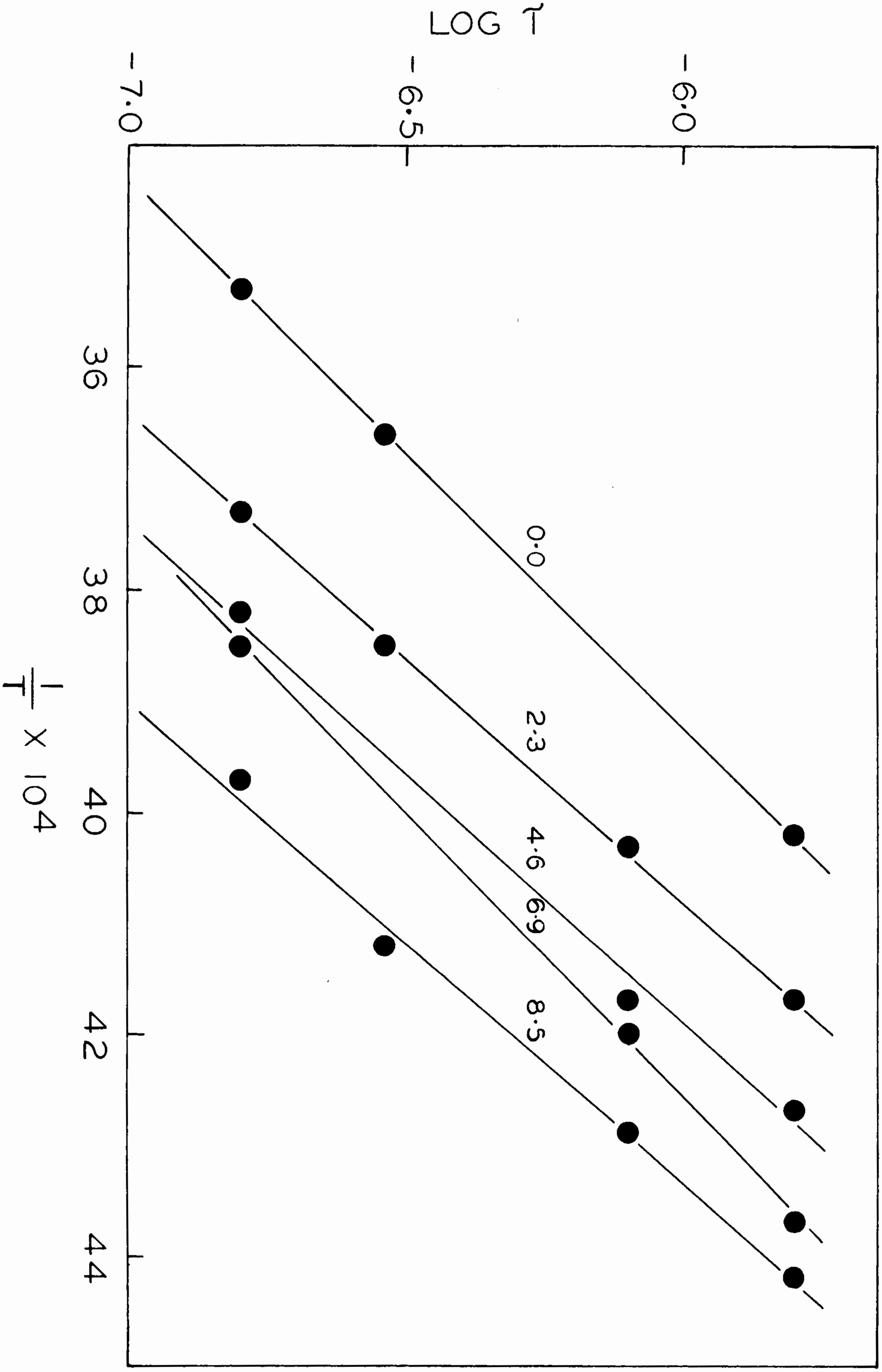
Log τ versus 1/T for paper containing 0.0, 2.3, 4.6, 6.9, and 8.5% adsorbed ethanol.



LOG τ
-6.0
-6.5
-7.0
$\frac{1}{T} \times 10^4$
36
38
40
42
44
0.0
3.3
5.3



LOG τ
-6·0
-6·5
-7·0
36
38
40
42
44
$\frac{1}{T} \times 10^4$
0·0
1·7
2·5
3·2
3·9
5·4
7·0
1
2
3
4


LOG τ
-6.0
-6.5
-7.0
36
38
40
42
44
1/T × 10⁴
0·0
2·3
4·6
6·9
8·5

These values of τ as well as of σ, ΔF^{*}, ΔH^{*}, and ΔS^{*} are presented in Table XXV.

Let us first consider the data for methanol. The variation of each of ΔF^{*}, ΔH^{*}, and ΔS^{*} with % adsorbed methanol is shown in Figure 21. Following directly from the trends in τ, ΔF^{*} is seen to decrease quite rapidly at first, levels off in the range 3 to 4% and then proceeds to decrease further although not nearly so rapidly as previously. On the other hand, both ΔH^{*} and ΔS^{*} go through a pronounced maximum at 2.7%.

A glance at Table XXV indicates that the data for water in all probability shows similar trends, ΔH^{*} and ΔS^{*} passing through maxima quite close to 2.7%. These trends are observed as well for ethanol, as indicated in Figure 22.

At 2.7% then the restriction to dipole rotation is at a maximum in all three cases. It is interesting that at this same point (for water) the density as well as both refractive indices of native fibres likewise have a maximum value (33). One might expect the same to be the case for methanol and ethanol. Perhaps the decrease in height of the ΔH^{*} and ΔS^{*} curves as one procedes from water to methanol reflects a corresponding decrease of the density effect in the three cases.

The picture, however, is not complete. It is necessary to reconcile the absence of a maximum in the ΔF^{*} curve together with its presence in the corresponding curves for ΔS^{*} and ΔH^{*}. Similar non-parallelism in the trends of the three quantities has been frequently observed in chemical reactions in solution and is characteristic of phase changes (56). Large parallel changes in both ΔH^{*} and ΔS^{*} for the most

TABLE XXV

Evaluation of Free Energy, Enthalpy & Entropy of Activation for Relaxation for Paper at 298°K.

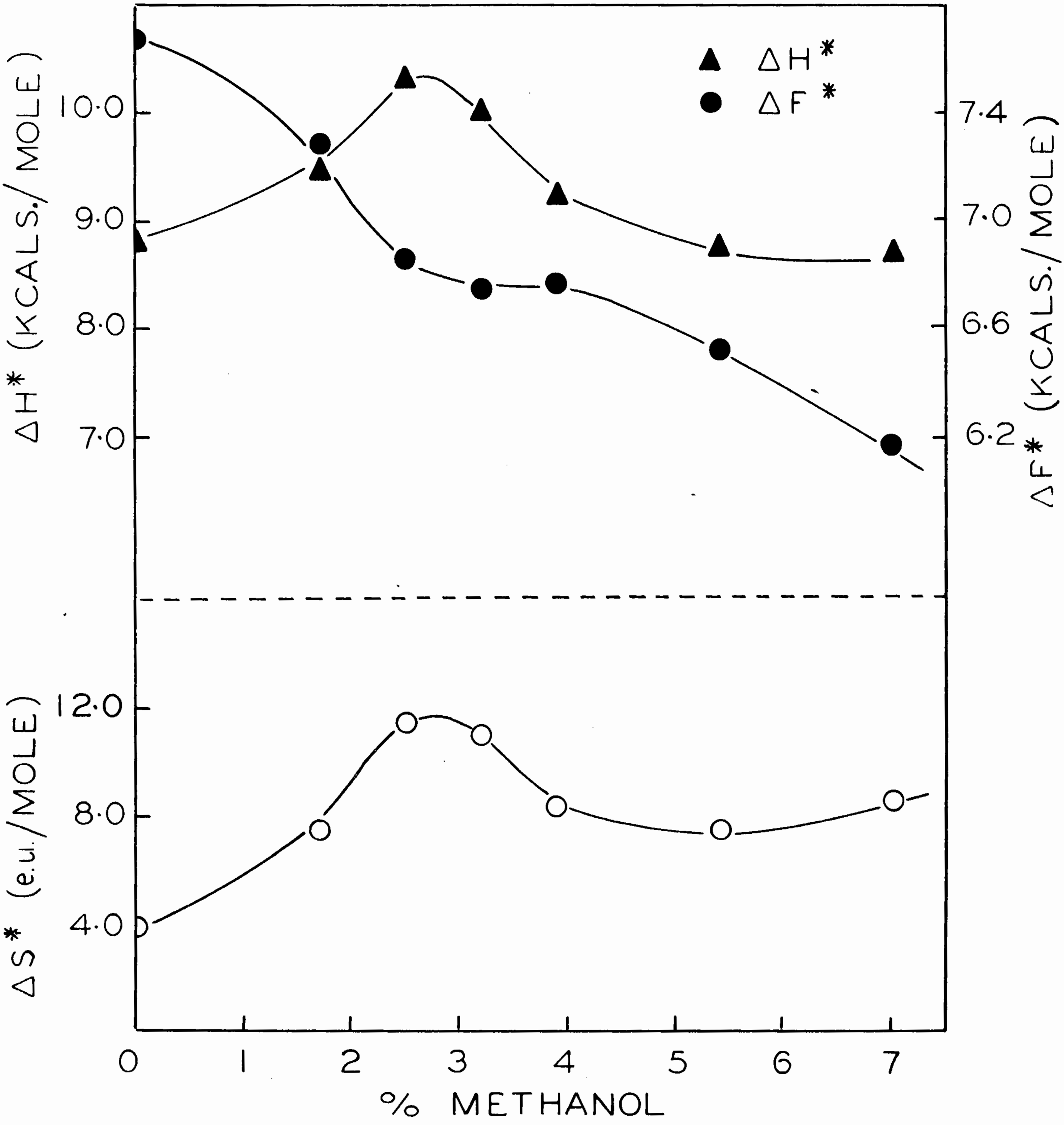
% Adsorbed Water (gms./gm. dry paper)	$\tau \times 10^{9}$ (secs.)	σ	$\Delta H^{\ast}$ (kcals./mole)	$\Delta F^{\ast}$ (kcals./mole)	$\Delta S^{\ast}$ (e.u.)
0.0	69.2	2060	8.84	7.68	3.9
3.3	8.2	2700	11.76	6.42	17.9
5.3	7.0	2200	9.48	6.33	10.6
% Adsorbed Methanol					
0.0	69.2	2060	8.84	7.68	3.9
1.7	35.5	2210	9.50	7.28	7.5
2.5	17.4	2380	10.30	6.86	11.5
3.2	14.4	2320	10.00	6.75	11.0
3.9	15.0	2160	9.27	6.77	8.4
5.4	9.9	2040	8.76	6.53	7.5
7.0	5.4	2040	8.72	6.17	8.6
% Adsorbed Ethanol					
0.0	69.2	2060	8.84	7.68	3.9
2.3	20.4	2350	10.16	6.95	10.8
4.6	14.6	2220	9.57	6.76	9.4
6.9	15.1	2020	8.65	6.78	6.3
8.5	5.5	2320	10.02	6.18	12.9

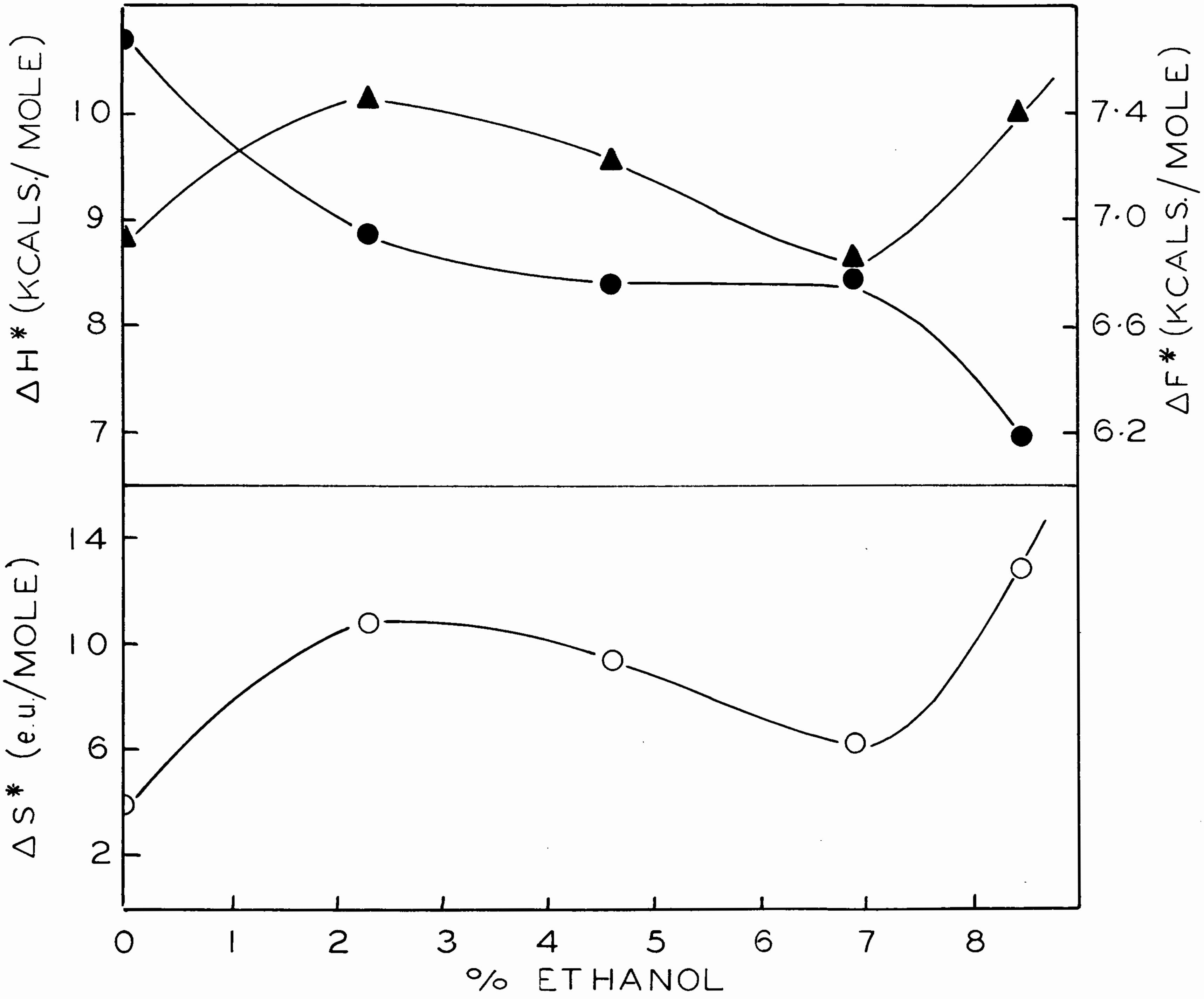
FIGURE 21

Variation with % adsorbed methanol of ΔH^{*}, ΔF^{*}, and ΔS^{*} for dielectric relaxation for paper at 298°K.

FIGURE 22

Variation with % adsorbed ethanol of ΔH^{*}, ΔF^{*}, and ΔS^{*} for dielectric relaxation for paper at 298°K.


▲ ΔH*
● ΔF*
ΔH* (KCALS./MOLE)
10·0
9·0
8·0
7·0
ΔF* (KCALS./MOLE)
7·4
7·0
6·6
6·2
ΔS* (e.u./MOLE)
12·0
8·0
4·0
0
1
2
3
4
5
6
7
% METHANOL


ΔH* (KCALS./ MOLE)
10
9
8
7
ΔF* (KCALS./ MOLE)
7·4
7·0
6·6
6·2
ΔS* (e.u./MOLE)
14
10
6
2
0
1
2
3
4
5
6
7
8
% ETHANOL

part compensate each other so that $\Delta F^{\ddagger}$, and consequently the reaction rate, remains very nearly the same.

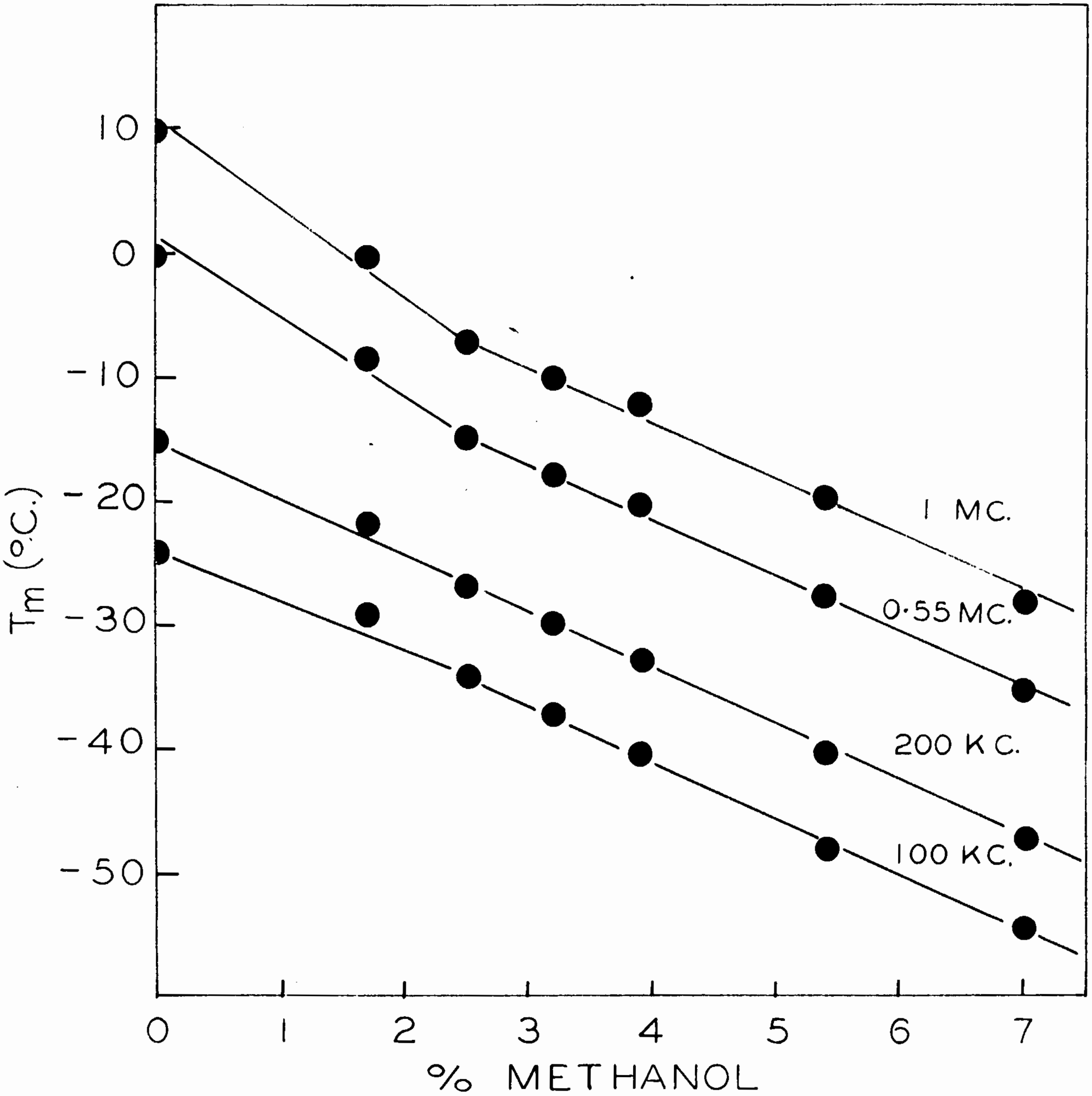
The dielectric relaxation process investigated here may then logically be considered to occur as follows, still referring to Figure 21. At the maximum point in the $\Delta S^{\ddagger}$ curve a maximum number of bonds must be broken per orientation of a single dipole. The enthalpy necessary is also at a maximum, but it is possible at the same time that the amount per bond broken may be less than for lower vapor contents. This is to be expected, in fact, on the assumption that the rotating dipoles are hydroxyl groups and that the hydroxyl groups of the sorbed vapor are also rotating. For it is well known that heats of wetting of cellulose become progressively smaller with increase in moisture content (64). One may then argue that the relaxation time is a function of the enthalpy increase per bond broken per rotation as well as of the number of bonds broken, or in other words, a function of the free energy increase. At vapor contents higher than that corresponding to the maximum point, the overall density of the cellulose system decreases and the number of broken bonds per dipole orientation, in other words, $\Delta S^{\ddagger}$, suffers a corresponding decrease. At the same time, the enthalpy increase per bond broken becomes even smaller so that there is a corresponding decrease in relaxation time.

In the above sense then water as well as methanol and ethanol may be considered as having in cellulose a plasticizing action similar to that observed in other polymer systems (11, 22, 23, 52).

The distinctness of the vapor content of 2.7% is manifested

FIGURE 23

Variation of T_m with % adsorbed methanol at the inscribed frequencies.



10
0
-10
-20
-30
-40
-50
Tm (°C.)
0
1
2
3
4
5
6
7
% METHANOL
1 MC.
0·55 MC.
200 KC.
100 KC.

in yet another fashion. When T_m is plotted versus % methanol for each of the four experimental frequencies, one obtains the plots of Figure 23. These plots are linear with a discontinuity at 2.5%. Above this point the slope is the same for all the frequencies, the deviation from the average being less than 1%. Below 2.5% on the other hand the slope undergoes a marked increase with decrease in frequency. In order to ensure better illustration of the relationships the points were taken from the log τ versus 1/T lines of Figure 19 rather than directly from the experimental data.

The plots are described by the following equations, T_m being expressed in degrees absolute:

$$T_m = K_1(\%\text{MeOH}) + K_2 ; \quad \%\text{MeOH} < 2.5$$

$$T_m = -4.54\ (\%\text{MeOH}) + K_3 ; \quad \%\text{MeOH} > 2.5$$

In Table XXVI are presented the values of K_1, K_2, and K_3 for the different frequencies.

Effect of Vapor Content on Increase in Loss Maximum

For the case of a single relaxation time τ, the maximum value of ϵ'' is given by (48):

$$\epsilon''_{max} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2 \mu^2 n$$

where k is the Boltzmann constant = 1.38×10^{-16} erg/degree, T is the absolute temperature, ϵ_0 is the static dielectric constant, and n is the

TABLE XXVI

Evaluation of constants for the plots of Figure 23

Frequency (kcs.)	K_1	K_2	K_3
100	-4.06	249.0	250.2
200	-4.54	258.0	258.0
550	-6.09	273.7	269.7
1000	-7.26	284.6	277.3

number of dipoles per cc. μ is the dipole moment, assumed to be 1.7 x 10^{-18} e.s.u. for the hydroxyl group (48). $d\epsilon''_{max}/dn$ is given by:

$$\frac{d\epsilon''_{max}}{dn} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2 \mu^2$$

assuming no change in T or ϵ_0. In this way a loss value is assigned to a single adsorbed dipole in one cc. of material. In order to be consistent with the convention of expressing the amount of adsorbed vapor in terms of grams per 100 grams of dry material, a loss value is assigned to one gram of adsorbed dipole per 100 grams dry material as follows:

$$\frac{d\epsilon''_{max}}{dn_c} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2 \mu^2 \frac{Nd}{100M}$$

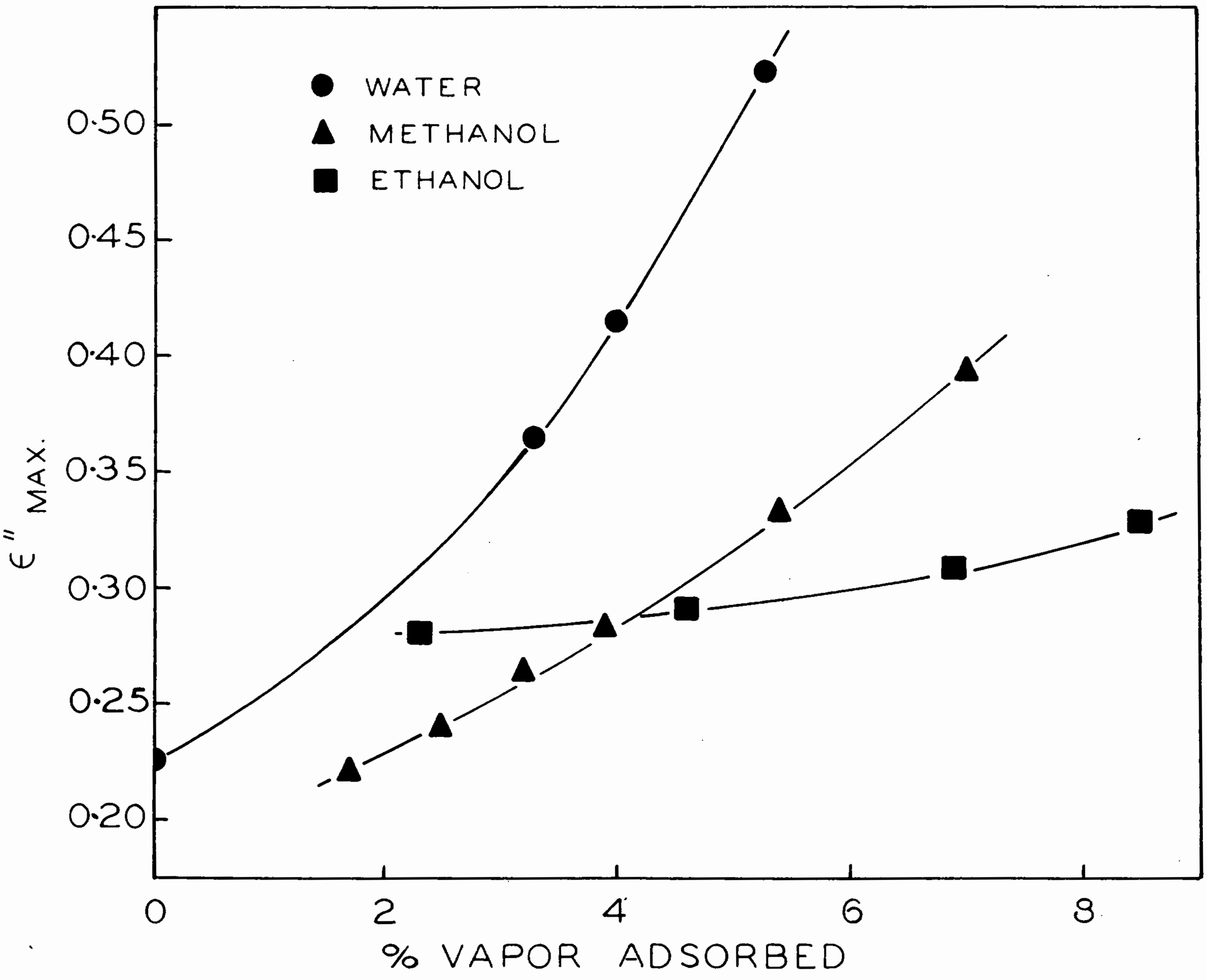
where N is Avogradro's number, M is the weight of N dipoles, and d is the density of the material.

$d\epsilon''_{max}/dn_c$ may be obtained experimentally as well, as indicated in the Results. However, as emphasized before, the linear plots of Figure 14 describe the compound dielectric cellulose-vapor -- vapor, whereas data for cellulose itself are desired for purposes of comparison.

This is obtained as follows: the requisite ϵ''_2 data was transformed to ϵ''_1 by the method described in Analysis of Dielectric. It has been shown that the dissipation factor of a paper sheet is roughly directly proportional to its density (8, 16). With this relation ϵ''_1 was transformed to ϵ'' for the cellulose fibre itself, using the density values of Table $\overline{\underline{XXIV}}$. The requisite data is shown in Table $\overline{\underline{XXVII}}$ and

FIGURE 24

ϵ''_{max} for the cellulose fibre: its variation with vapor content.



WATER
METHANOL
ETHANOL
0·50
0·45
0·40
0·35
0·30
0·25
0·20
ε″ MAX.
0
2
4
6
8
% VAPOR ADSORBED

plotted in Figure 24. The plots are slightly curved, the curvature being greatest in the case of water. This is no doubt a consequence of the fact that T decreases and ϵ_0 increases with increase in vapor content, the combined effect being greatest for water, presumably. From the slopes of these curves (at 5.3% vapor content) values of $d\epsilon''_{max}/dn_c$ were computed; these are presented in Table XXVIII together with those obtained from the above equation, as well as the corresponding values for crystalline and amorphous terylene. It ought to be pointed out here that by crystalline terylene is meant the normally occurring substance, which has a crystalline fraction of about 0.4 (48). ϵ_0 for dry cellulose was taken as 6.

It will be noticed that in all cases in this table the experimental value of $d\epsilon''_{max}/dn_c$ is much smaller than the theoretical. This can undoubtedly be explained on the basis of a spread of relaxation times as a consequence of which the measured ϵ''_{max} is considerably lower than the theoretical value (38). Even so, the reported experimental values for cellulose are probably a little high as a result of the slight magnifying effect of a decrease in temperature on ϵ''_{max}. Here one assumes of course the correctness of the model used in calculating ϵ''_{max}. Theoretically, one would expect $d\epsilon''_{max}/dn_c$ to be considerably less for terylene-water than for cellulose-water because of smaller values for ϵ_0 and d. That this is so experimentally is evidence in favour of the assumption referred to above. The effect of changes in ϵ_0 and d is manifested as well in the smaller value of $d\epsilon''_{max}/dn_c$ for crystalline terylene than for the amorphous modification.

TABLE XXVII

ϵ''_{max} for the cellulose fibre: its variation with vapor content

% Vapor	T_m	ϵ''_{2max}	ϵ'_2	ϵ'_1	ϵ''_1	ϵ'	ϵ''
Water							
0.0	10	.0160	1.306	1.598	.02740	4.24	.227
3.3	-12	.0218	1.353	1.707	.03892	5.22	.365
4.0	-17	.0233	1.372	1.751	.04225	5.66	.415
5.3	-21	.0262	1.404	1.828	.04885	6.52	.522
Methanol							
1.7	- 8	.0158	1.323	1.620	.02680	4.35	.222
2.5	-15	.0171	1.328	1.629	.02903	4.41	.241
3.2	-16	.0179	1.342	1.661	.03082	4.68	.265
3.9	-19	.0190	1.350	1.675	.03275	4.79	.284
5.4	-26	.0212	1.369	1.716	.03701	5.14	.334
7.0	-35	.0232	1.394	1.773	.04135	5.68	.394
Ethanol							
2.3	- 5	.0198	1.328	1.629	.03362	4.43	.281
4.6	-12	.0210	1.338	1.643	.03554	4.46	.292
6.9	-13	.0222	1.351	1.668	.03784	4.56	.309
8.5	-21	.0231	1.366	1.700	.03975	4.78	.329

TABLE XXVIII

$d\epsilon''_{max}/dn_c$ -- Theoretical and experimental values for cellulose and terylene

Material	Theoretical	Experimental	Theoretical/ Experimental
Terylene (amorphous)	0.245	0.0488	5.02
Terylene (crystalline)	0.232	.0433	5.35
Cellulose + water	.676	.0834	8.10
Cellulose + methanol	.676	.0638	10.6
Cellulose + ethanol	.676	.0206	32.8

SUMMARY AND CONCLUSIONS

Water is known to have a pronounced softening effect on cellulose. The dielectric relaxation time (τ) of a substance, together with related properties, may be considered as a measure of the facility with which its dipoles can rotate in an alternating electric field. It would be expected then that in cellulose τ would be affected to a greater or lesser extent by the presence of adsorbed water and similar vapors.

It was found convenient to perform experiments with quantitative filter paper inserted in the measuring condenser in a wrap-around fashion. The necessity thus arose for determining whether or not relaxation times for this arrangement corresponded to those for the paper itself. Electrical analysis showed that there was no deviation within experimental error. Using the equations obtained calculations were made of the dielectric constant and maximum dielectric loss factor of the cellulose fibre as a function of per cent adsorbed water, methanol, and ethanol, respectively, this being the order of decreasing effect. The value of the dielectric constant for dry cellulose was in agreement with that obtained by previous workers.

It was found that water, as well as methanol and ethanol, caused the relaxation time at 298° K. to decrease. In all three cases the curve of ΔH^{*} and ΔS^{*} versus vapor content passed at about 2.7% vapor content through a maximum, the height of which decreased in the order water, methanol, and ethanol. This was correlated with the fact that the curve of cellulose density versus water content passes through a maximum at this very point. It was predicted that the corresponding density curves for methanol and ethanol would run a similar course, the heights decreasing in the same order as for the ΔH^{*} and ΔS^{*} curves. Thus it was shown that water, methanol, and ethanol have in cellulose a plasticizing action comparable with that observed in other plasticized polymer systems.

CLAIMS OF ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

1. Values of dielectric constant and dielectric loss factor were obtained in a dispersion region for a complex arrangement in the measuring condenser of a paper made of pure cellulose. Measurements were performed over a range of frequency of 10 to 1000 Kc. and a range of temperature of -58 to 26°C.
2. It was shown by electrical analysis that the position of the dispersion region thus obtained was not altered upon consideration of the data in terms of the paper itself.
3. From equations obtained as a result of this analysis calculations were made of the dielectric constant of the cellulose fibre at 1 Mc. and 20°C. as a function of per cent adsorbed water, methanol, and ethanol, respectively.
4. In the same way the corresponding maximum dielectric loss factor was calculated as a function of vapor content, the slopes of the curves being considered as a measure of the losses due to the hydroxyl groups in the adsorbed vapor.
5. From the maxima in the loss curves relaxation times were evaluated. From plots of log τ versus $1/T$, calculations were made at 298°K. of the free energy, enthalpy, and entropy of activation for dielectric relaxation, these terms being considered as a function of vapor content.

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