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## Dielectric Properties of Wool-Water Systems. II. 26 000 Megacycles

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The complex dielectric constant for wool-water systems has been determined at a frequency of 26 000 Mc by a cavity resonator method similar to the method employed at 3000 and 9300 Mc. At 26 000 Mc, measurements on single wool fibers and at relative humidities as high as 98% have proved feasible.

The complex dielectric constant of the wool-water system increases with increasing water content. Curves for the dielectric constant and loss factor of the wool-water systems at 26 000 Mc are presented and analyzed in terms of a new theory of water sorption by wool. According to this theory, which is based upon a theory originally proposed by Cassie, the water sorbed by wool consists of three distinct molecular species: (1) localized water irrotationally bound to polar sites in the wool, (2) mobile water with bulk liquid properties, and (3) intermediate water with a potential energy of absorption which lies between those for localized and mobile water. The analysis of the measurements at 26 000 Mc for the higher relative humidities in terms of this theory has resulted in a more thorough description of the properties of the sorbed water than was possible for the data obtained at 3000 and 9300 Mc.

THE present paper is a sequel to an earlier paper on the dielectric properties of wool-water systems at 3000 and 9300 Mc.<sup>1</sup> In I the attempt was made to explain the observed variation of the complex dielectric constant of wool-water systems by considering the sorbed water to be composed of two distinct dielectric species: (1) localized water intimately bound to low-energy sites in the wool and (2) mobile water sorbed under attractive forces like those in liquid water. This approach was based upon the work of Cassie,<sup>2</sup> in which the theory of multimolecular absorption was applied to the absorption of water by wool. From the results of this work it was possible to determine the amounts of localized and mobile water present at any water content. With these data and the formulas for the dielectric constants and loss factors of polar mixtures developed in I, the dielectric properties of the localized and mobile water were determined from the dielectric properties of the wool-water mixture. The value obtained for the dielectric constant of the localized water was found to be in close agreement with the microwave dielectric constant for irrotationally bound water of Buchanan *et al.*<sup>3</sup> obtained from studies of protein hydration. The complex dielectric constant of the mobile water, however, at both frequencies, was found to be less than that for bulk water at the same frequencies. Attempts to allow the dielectric properties of the wool to vary with water content so that the dielectric properties of the mobile water could be set equal to that of the bulk liquid failed. This result was interpreted as indicating that the dielectric properties of the wool can be considered to be essentially independent of water content at these frequencies, and that up to 14% water content (the maximum water content at which these measure-

ments were made) the mobile water is attracted with forces greater than those in liquid water.

In this paper the results of dielectric measurements at 26 000 Mc are presented. At this frequency and using single wool fibers<sup>4</sup> it has been possible to extend the measurements to water contents as high as 28% of the weight of the dry wool (98% R.H.). At the higher water contents the failure of Cassie's theory to account for the experimental results has led to the formulation of a new theory of the sorption of water by wool. This has permitted a more thorough investigation to be made of the dielectric properties of the sorbed water.

## THEORY

The expression for the dielectric constant of a mixture of dielectrics, as it was given in I is

$$\frac{(\epsilon' - 1)(2\epsilon' + 1)}{9\epsilon'} \frac{\sum_i M_i X_i}{\rho} = \sum_i P_i X_i, \quad (1)$$

where  $M_i$ ,  $X_i$ , and  $P_i$  are the molecular weight, mole fraction, and molar polarization of the  $i$ th component and  $\epsilon'$  and  $\rho$  are the dielectric constant and density of the mixture.

The dielectric loss factor for a mixture of dielectrics is given by the expression

$$\epsilon'' = \sum_i \epsilon_i'' v_i, \quad (2)$$

where  $\epsilon''$  is the dielectric loss factor of the mixture and  $\epsilon_i''$  and  $v_i$  are the dielectric loss factor and volume fraction of the  $i$ th component.<sup>5</sup> The equation for the

<sup>4</sup> J. J. Windle and T. M. Shaw, Textile Research J. 25, 865 (1955).

<sup>5</sup> The mean power absorbed by a specimen of volume  $V$  and dielectric conductivity  $\sigma$  in an electric field of strength  $E$  is given by

$$W = \frac{1}{2} \int_V \sigma E^2 dv, \quad (a)$$

where  $dv$  is the incremental volume element. When the specimen is everywhere in a region of constant field equation (a) becomes simply

$$W = \frac{1}{2} \sigma E^2 V. \quad (b)$$

For a dielectric composed of a mixture of dielectrics each with a

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<sup>1</sup> J. J. Windle and T. M. Shaw, J. Chem. Phys. 22, 1752 (1954). This article will be referred to hereafter as I.

<sup>2</sup> A. B. D. Cassie, Trans. Faraday Soc. 41, 458 (1945).

<sup>3</sup> Buchanan, Haggis, Hasted, and Robinson, Proc. Roy. Soc. (London) A213, 379 (1952).

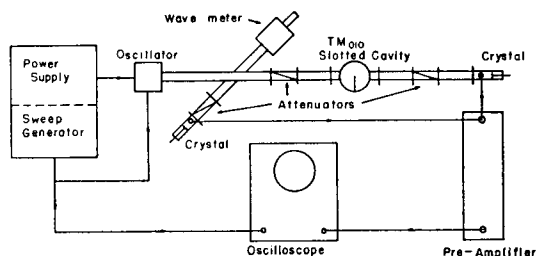


FIG. 1. A block diagram of the microwave test setup employed at 26 000 Mc for the determination of the complex dielectric constant of single wool fibers.

dielectric loss factor as it appears in I is incorrect because mole fractions were used instead of volume fractions. The correct form for the equation when using mole fractions is

$$\epsilon'' = \frac{\rho \sum_i (M_i / \rho_i) X_i \epsilon_i''}{\sum_i M_i X_i}, \quad (2a)$$

where the meanings of the terms are the same as in Eq. (1). Although the use of the correct equation changes somewhat the values calculated in I for the dielectric loss factors of the sorbed water the discussion based upon the results in I remains unchanged.

### The Wool-Water System

The wool-water system in I was depicted as a mixture composed of wool, localized water, and mobile water. In the present work, it has been necessary to enlarge this picture to include in the subdivision of the sorbed water a third, intermediate fraction. In this analysis, the assumptions have been made that the localized molecules are sorbed onto low-energy sites with a potential energy much greater than the potential energy of molecules in the bulk liquid and that the potential energy of the mobile molecules is the same as that for molecules in the bulk liquid. The additional assumption has been made that there are some molecules sorbed with a potential energy somewhere intermediate to the potential energies of the localized and mobile molecules. In terms of this picture of the wool-water system, the dielectric results of the present work are analyzed by means of Eqs. (1) and (2a). The arguments in favor of this analysis, as well as the details of the statistical thermodynamics of the system and the calculations giving the distribution of the sorbed water among the three energy states at any water content, are discussed elsewhere.<sup>6</sup>

dielectric conductivity  $\sigma_i$  and a volume  $V_i$  in a region of constant field, the mean power absorbed will be given by

$$W = \sum_i W_i = \frac{1}{2} E^2 \sum_i \sigma_i V_i. \quad (c)$$

Equating Eqs. (b) and (c) and recalling that  $\sigma = \omega \epsilon''$  where  $\omega$  is the circular frequency we get

$$\epsilon'' = \sum_i \epsilon_i'' v_i$$

where  $v_i = V_i/V$  the volume fraction. This is Eq. (2) of the text.

<sup>6</sup> J. J. Windle, *J. Polymer Sci.* (July, 1956).

### EXPERIMENTAL

A schematic diagram of the microwave test setup employed at 26 000 Mc is shown in Fig. 1. The microwave energy is obtained from a Raytheon QK 277 Klystron. The cavity is isolated from the oscillator and detector by suitable attenuators. The preamplifier has a differential input balanced to ground. This permits the output of both the cavity and wave meter to be displayed in opposition simultaneously upon the oscilloscope. A single wool fiber causes a frequency shift of the order of 5 Mc which can be measured with a precision of about 2% by means of the absorption-type wave meter equipped with an optical lever.

The methods used for the determination of  $\epsilon'$ , the dielectric constant, and  $\epsilon''$ , the dielectric loss factor, are exactly the same as those employed in I. However, the technique employed in I of mounting the fibers in a holder which could be humidified in a vacuum desiccator could not be employed with the single fiber specimens because within the time required to transfer a single fiber from a desiccator to the cavity and make a measurement, the fiber lost its conditioning and equilibrated itself with the room humidity. The small size of the cavity resonator, however, made it possible to enclose the cavity and fiber specimen in a simple humidity chamber as is shown in Fig. 2. Desiccant, or the appropriate mixture of sulfuric acid and water placed in a dish in the bottom of the chamber provided the desired relative humidity. The cavity resonator was sealed from the external atmosphere by Teflon windows at the wave-guide joints. The fiber was held taut by a small brass weight attached to one end and could be moved in and out of the cavity by means of a small Alnico magnet (shown on top of the chamber in Fig. 2) which attracted a steel clip attached to the other end of the fiber. The water content of the fibers was determined from the sorption isotherm for wool. Equilibrium between the fiber specimen and the atmosphere of the chamber was considered to have been achieved when

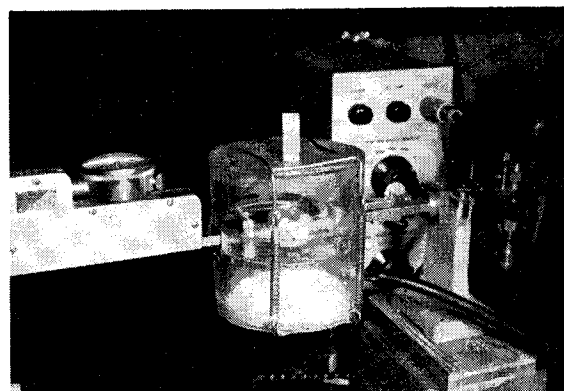


FIG. 2. Close-up photograph of the resonant cavity enclosed in the humidity chamber. The rectangular block on top of the chamber is a small Alnico magnet used to remotely move the fiber in and out of the cavity. The fiber, mounted between two clips, can be seen inserted in the slot in the cavity.

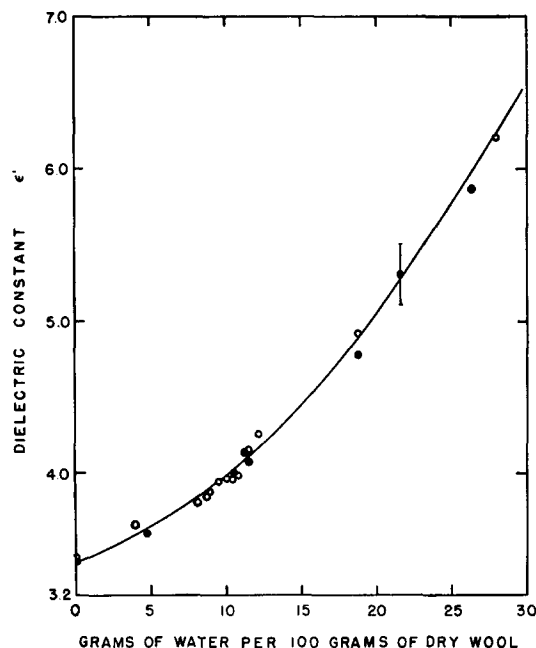


FIG. 3. A comparison of the experimental values of the dielectric constant of the wool-water systems for two different fibers (open and closed circles) with the theoretical relationship (solid curve) calculated from Eq. (3). The radius of the circles represents the estimated uncertainty in the water content and the vertical line represents an experimental error of approximately 4% in the dielectric constant.

the change in resonant frequency caused by the specimen remained constant. Equilibrium was reached within a few hours with the single fiber specimens. No noticeable change was observed in the equilibrium condition with improved circulation of the atmosphere within the chamber by stirring. All measurements were made at a temperature of 25°C.

## RESULTS AND DISCUSSION

### Dielectric Constant

The results of a number of dielectric constant determinations at various water contents between 0 and 28% on two different wool fibers are shown in Fig. 3. The radius of the circles representing the experimental points indicate the uncertainty in the water content. The vertical line through one of the points indicates the estimated experimental error of approximately 4% in the dielectric constant.

The dielectric constant of the wool-water system is, according to Eq. (1), given by the expression

$$\frac{(\epsilon' - 1)(2\epsilon' + 1)}{9\epsilon'} \frac{M_K X_K + M_W X_W}{\rho} = P_K X_K + P_l X_l + P_s X_s + P_m X_m, \quad (3)$$

where  $M_K$  and  $M_W$  are the average molecular weights of the amino acid residues in wool, and the sorbed water,

respectively,  $P_K$ ,  $P_l$ ,  $P_s$ ,  $P_m$  are the molar polarizations of the dry wool, localized water, intermediate water, and mobile water, respectively, and  $X_K$ ,  $X_l$ ,  $X_s$ ,  $X_m$  are the corresponding mole fractions of these components ( $X_W = X_l + X_s + X_m$ ). The values of the mole fractions of the sorbed water components have been determined by means of the new theory from an analysis of the reduced vapor pressure isotherm for wool. The solid curve in Fig. 3 was calculated by means of Eq. (3) using the values of  $P_K$ ,  $P_l$ ,  $P_s$  and  $P_m$  given in Table I. The value of  $P_K$  was calculated from the value of  $\epsilon_K'$  as measured for the dry wool.  $P_m$ , as required by the theory, was set equal to the value for the polarization of bulk water at 26 000 Mc. The values of  $P_l$  and  $P_s$  were obtained by a least-squares calculation from the best smoothed curve passed through experimental points of Fig. 3. The polarization of the localized water corresponds to a dielectric constant of about 4.5. This value is in substantial agreement with the high-frequency dielectric constant of water and supports the arguments made in I concerning the nature of the localized water. The value for the polarization of the intermediate water appears to be plausible since it falls between the values for localized and bulk water.

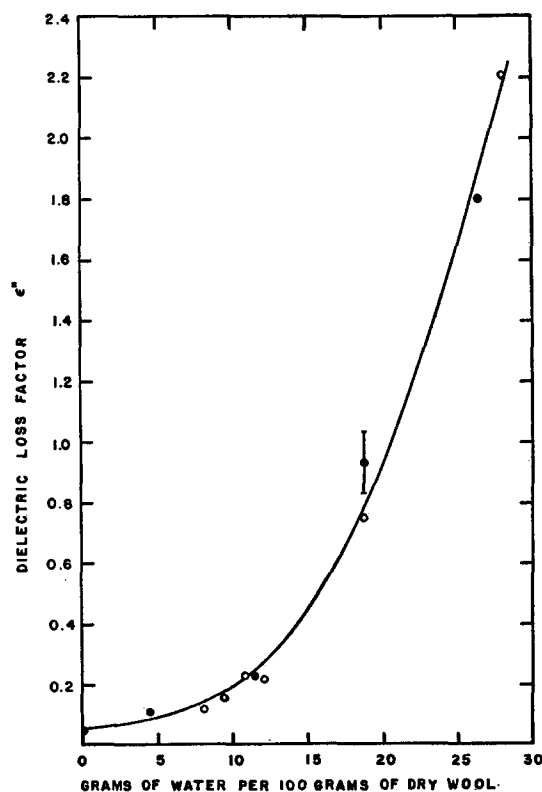


FIG. 4. A comparison of the experimental value of the dielectric loss factor of the wool-water systems for two different fibers (open and closed circles) with the theoretical relationship calculated from Eq. (4) for localized, intermediate, and mobile water (solid curve).

### Dielectric Loss Factor

The variation of the dielectric loss factor for wool-water systems at 26 000 Mc is shown in Fig. 4. These measurements were made upon the same fibers used in the dielectric constant determinations, and over the same water content range. At this frequency the dielectric loss factor for the dry wool is too small to measure precisely by the methods employed here. The experimental value of 0.05 for  $\epsilon_K''$  shown in Fig. 4 probably represents an upper limit subject to an estimated uncertainty of about 20%. The uncertainty in the remainder of the points is estimated to be only 10%.

The dielectric loss factor for the wool-water system is given, according to Eq. (2), by the expression

$$\epsilon'' = \epsilon_K'' v_K + \epsilon_I'' v_I + \epsilon_s'' v_s + \epsilon_m'' v_m, \quad (4)$$

where the subscripts have the same meaning as in the expression for the dielectric constant. Equation (4) was used to evaluate the dielectric loss factors of the localized and intermediate water by means of a least-squares calculation from the best smoothed curve through the experimental points of Fig. 4. The dielectric loss factor for the dry wool was obtained from the measurement at zero water content and, as required by the theory, the dielectric loss factor of the mobile water was set equal to that for the bulk liquid at this frequency. The values for the dielectric loss factors for all of the components are given in Table II.

The value of 0.16 for the dielectric loss factor of the localized water is consistent with values for the high-frequency dielectric loss factor due to resonance absorption of liquid water and thus is in accord with the discussion in I concerning the dielectric properties of the localized water. The dielectric loss factor for the intermediate water also appears to be plausible. The solid curve of Fig. 4 has been calculated by means of Eq. (4) using the dielectric loss factor values given in Table II. The close agreement between the calculated curve and the experimental points over the whole water content range is considered to confirm the present analysis.

### Localized Water

The dielectric properties of the localized water in I and in the present work support the picture of localized water as visualized in the theory of multimolecular absorption. In this picture, the localized water is composed of a random distribution of water molecules irrotationally bound with equal energy of absorption to

polar sites throughout the wool fiber. The dielectric properties of this water should be very much like the dielectric properties of bulk water measured at very high frequencies and in the absence of any Debye absorption; the complex dielectric constant found for the localized water corresponds very closely to this picture.

### Mobile Water

The theories of water sorption by wool employed in I and in the present work require that the molecules of mobile water be sorbed with a potential energy identical to that for molecules in the bulk liquid. This means that the mobile water must have the same dielectric properties as the bulk liquid. In I, however, agreement between the theory and experiment could be obtained only with dielectric properties for the mobile water less than those for the bulk liquid. We have suggested that this discrepancy is due to the assumption in the sorption theory used in I that all the molecules sorbed in addition to the localized molecules are identical and have the same properties as the bulk liquid. A more likely assumption, as the dielectric results of I have indicated, is that at least some of these molecules are more strongly sorbed and have intermediate properties. The theory employed in the present work is an attempt to take this into account by introducing a third, intermediate species of water molecule. With this assumption it is now possible to set the dielectric properties of the mobile water equal to those for bulk liquid. The good agreement obtained between the experimental results and the theory, and the fact that a plausible result has been obtained for the complex dielectric constant of the intermediate water, is taken as confirmation of the correctness of this analysis.

### Intermediate Water

The only condition placed upon the intermediate water by the sorption theory is that its potential energy of sorption be somewhere intermediate between localized water on one extreme and mobile water on the other. The partition function for the intermediate water was found upon analysis of the reduced isotherm to be in accord with this condition. As a consequence of this condition, the dielectric properties of this fraction also must lie between those for the localized and mobile water. In the analysis of the dielectric data, this was found to be the case. The values obtained for the dielectric properties were quite plausible and they indicate that the mobile water is more mobile in char-

TABLE I. Polarization of dry wool, localized water, intermediate water, and mobile water at 26 000 Mc.

$P_K$ (cc)	$P_I$ (cc)	$P_s$ (cc)	$P_m$ (cc)
55.4	15.0	72.6	98.0

TABLE II. The dielectric loss factors for dry wool, localized water, intermediate water, and mobile water at 26 000 Mc.

$\epsilon_K''$	$\epsilon_I''$	$\epsilon_s''$	$\epsilon_m''$
0.05	0.16	3.51	32.0

acter than localized. Without additional information<sup>7</sup> about the properties of the intermediate water, however, further discussion would be only speculative and will not be pursued.

### CONCLUSION

The results of the present experiments plus those of I and their interpretation in terms of a modification of the theory of water absorption by wool proposed by Cassie have led to a picture of water sorption by wool in which there occur simultaneously the sorption of localized water onto localized sites in the wool and the sorption of at least two other kinds of water which may be distinguished by their different energies of absorption. The good agreement with experimental observations obtained with this model however does

<sup>7</sup> More information about the properties of the intermediate water may be obtained by application of the present theory to the work of Hedges [Trans. Faraday Soc. 22, 178 (1926)] on the heat of wetting of wool and of Speakman [Trans. Faraday Soc. 25, 92 (1929)] on the elasticity of wool-water systems, since both of these authors have concluded from their experimental results that the water is sorbed by wool in three different ways. Such an analysis, however, most properly belongs in a discussion of the theory as applied to wool and will be reserved for that paper.

not necessarily mean that it is entirely correct; rather, it shows that, although the dielectric data appear to be more sensitive than the moisture isotherm as a test of a sorption theory (since agreement with the isotherm was obtained with a single species of mobile water whereas the dielectric data indicate that at least two species must be present) these data are, in their present state, still relatively insensitive. It would appear that the strong interaction between the absorber and the localized molecules must extend, diminishingly, to all sorbed molecules and that a more sensitive experiment would reveal many species of mobile water. A refinement of the dielectric measurements or some other entirely different type of measurement<sup>8</sup> may verify these conclusions.

### ACKNOWLEDGMENTS

The authors would like to thank Dr. K. J. Palmer for his interest and suggestions during the course of this work.

<sup>8</sup> Preliminary unpublished measurements on the variation of the proton magnetic resonance line width of sorbed water indicate that this technique may have promise in such a study.

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## Calculation of Vibrational Relaxation Times of the Chloromethanes\*

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The Schwartz, Slawsky, and Herzfeld method for the calculation of vibrational relaxation times of gases has been extended in its application to polyatomic molecules. A general method is developed for the calculation of the effective relaxation times and the associated constants of the sound velocity relaxation equation. Calculations have been made for the bimolecular collisions of methane and the chloromethanes involving changes of one, two, and three quanta. A normal coordinate treatment is used to obtain the atomic vibrational amplitudes. The effect of an intermolecular potential function, embodying a dipole interaction term, is included for the polar molecules of this investigation.

Calculated results are compared with experimental data. For CH<sub>4</sub> and CH<sub>3</sub>Cl the calculations agree well with experimental results. For CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> the calculated relaxation times are higher than selected experimental values by factors of 8-9. For CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> two major relaxation times are calculated. In the case of CH<sub>2</sub>Cl<sub>2</sub> the two relaxation areas have been observed. The experimental data on CHCl<sub>3</sub> and CCl<sub>4</sub> remain inconclusive in respect to the two predicted relaxation areas. Collisions involving three quanta are shown to be important for CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub>.

### I. INTRODUCTION

A THREE-DIMENSIONAL theory for the calculation of vibrational relaxation times of gases, based on molecular constants, has been developed in papers by Schwartz, Slawsky, and Herzfeld.<sup>1-4</sup> Calculations

have previously been made on diatomic and linear triatomic molecules. The method has now been further detailed for application to more complicated molecules and has been applied to methane and the chloromethanes. Calculated results are compared with available experimental data.

\* A dissertation submitted to the Faculty of the Graduate School of Arts and Sciences of the Catholic University of America in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>1</sup> Schwartz, Slawsky, and Herzfeld, J. Chem. Phys. 20, 1591 (1952); hereafter referred to as S.S.H.

<sup>2</sup> K. F. Herzfeld in F. D. Rossini, *Thermodynamics and*

*Physics of Matter* (Princeton University Press, Princeton, 1955), Sec. H, pp. 703-723.

<sup>3</sup> R. N. Schwartz, Ph.D. dissertation, Catholic University (1953).

<sup>4</sup> R. N. Schwartz and K. F. Herzfeld, J. Chem. Phys. 22, 767 (1954).