

Electrical Anisotropy of Xerogels of Hydrophile Colloids. Part II

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Citation: [The Journal of Chemical Physics](#) **12**, 513 (1944); doi: 10.1063/1.1723901

View online: <http://dx.doi.org/10.1063/1.1723901>

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where $G = E_V/hc$ is the vibrational term given in Eq. (28) and $F = E_R/hc$, if E_R is a root of the secular determinant (31). The selection rules allow all possible vibrational transitions because of the asymmetry of the molecular configuration. The selection rules for the rotational transitions and the calculations of the intensities of the rotational lines in the bands of asymmetric molecules have been discussed by Dennison,¹¹ Nielsen,¹⁵ and others.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 12, NUMBER 12 DECEMBER, 1944

Electrical Anisotropy of Xerogels of Hydrophile Colloids. Part II*†

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(Received October 5, 1944)

An improved, though still relative, quantitative expression has been derived for the electrical anisotropy E. A. The E. A. is a linear function of the elongation up to a certain limit, as is also the optical birefringence. The relation of electrical to optical anisotropy has been studied in greater detail. A more critical discussion in terms of atomic model structures is given of the hypothesis that E. A. in the compounds studied is due to the formation of continuous parallel chains of hydrogen bridges, having electronically conducting character. The materials studied were: polyvinyl acetate and its hydrolyzed stages down to polyvinyl alcohol, cellulose acetate and its hydrolyzed stages down to (hydrate) cellulose.

IN Part I the electrical anisotropy was expressed quantitatively in a quite relative form as ϕ/V^2h , where ϕ is the angle of rotation (from 45° as rest) by a field V , for a cylinder of unit radius and thickness h .**

MODIFICATION OF THE QUANTITATIVE EXPRESSION

It has been observed that the effect, for a disk not too large compared with the electrode, or pole-piece diameters, is an inverse linear function of the square of the distance between them, confirming the proportionality to V^2 . Further, it is found that the effect, other things being equal, is proportional to r^3 where r is the radius (cf. Fig. 1). Thus, it is proportional to the volume hr^2 , of the cylinder or disk, and again to the radius r , as defining the torque on the dipole of effective charge separation $2r$. To compare substances of different (monomeric) molecular weight, we can advance to the expression:

$$E. A. = K \cdot f(\Delta l/l) h r^3 V^2 d / M_m,$$

where K is an apparatus constant which can also

* Presented in the inaugural program of the Division of High-Polymer Physics, American Physical Society, Rochester, New York, June 23-24, 1944. For Part I, see J. Chem. Phys. 12, 244 (1944).

† Communication No. 997 from the Kodak Research Laboratories.

** Instead of t , used in Part I.

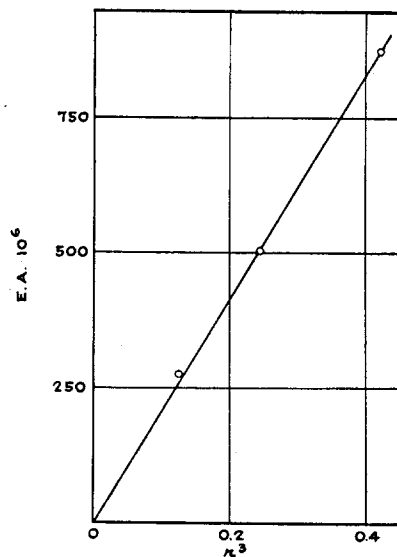


FIG. 1. Variation of electrical anisotropy of polyvinyl alcohol with the radius of the disk (200 percent elongation).

include Avogadro's constant, r =radius in cm, h =thickness, $f(\Delta l/l)$ is a function of the *elongation*, which reduces to proportionality for a certain range, V =voltage, d =specific gravity, and M_m ="equivalent" monomeric molecular weight.*

* E.g., $C_2(OH)$ for polyvinyl alcohol, $C_6(OH)_3$ for cellulose.

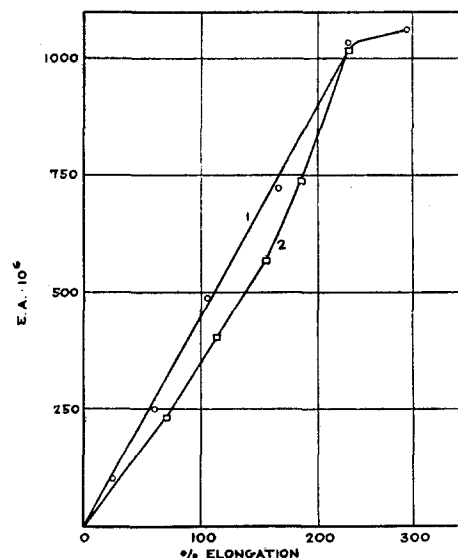


FIG. 2. Effect of elongation on electrical orientation of polyvinyl alcohol. 1. High viscosity. 2. Low viscosity.

ELONGATION

Since, usually, internal orientation or "fiber-ing" has been produced by stretching, the relation of E. A. to the amount of elongation to which the material has been subjected is important. This will be discussed in greater detail later; at this point it suffices to state that over a certain range, and with certain conditions maintained constant, the E. A. appears proportional to the actual elongation $\Delta l/l$, which, usually, will be expressed as a percentage. This is illustrated in Fig. 2. Fuller confirmation of the proportionality, up to some kind of elastic limit, is shown by the relation of the optical birefringence to the E. A.

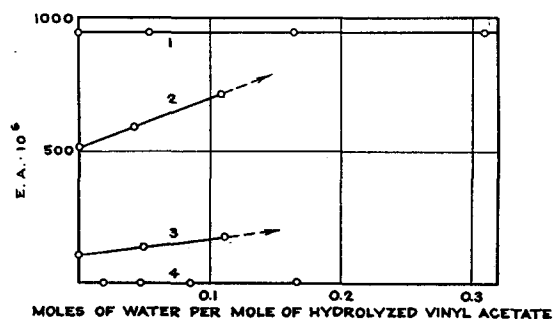


FIG. 3. Effect of water content on the electrical anisotropy of polyvinyl acetates at 225 percent elongation. 1. Polyvinyl alcohol. 2. Hydrolyzed polyvinyl acetate (73 percent polyvinyl alcohol). 3. Hydrolyzed polyvinyl acetate (35 percent polyvinyl alcohol). 4. Polyvinyl acetate.

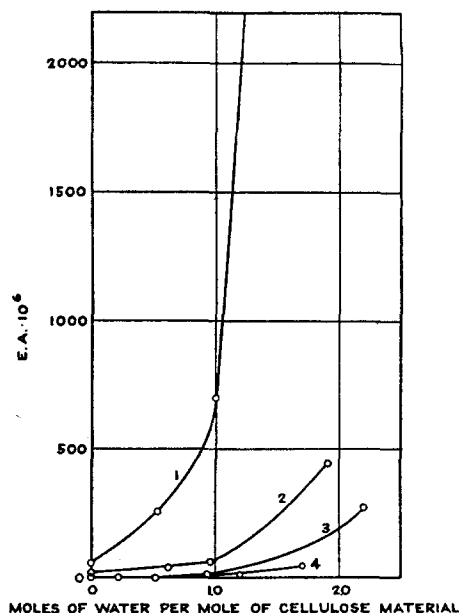


FIG. 4. Effect of water content on the electrical anisotropy of cellulose materials. 1. Cellulose, 0. 2. Cellulose acetate, 24.5 percent acetyl. 3. Cellulose acetate, 40.0 percent acetyl. 4. Cellulose acetate, 44.5 percent acetyl.

on the one hand, and to the elongation on the other (*vide supra*). These relations—of the linear regime to that beyond—are undoubtedly of great interest for the problems of structure and elasticity, but for the present we shall disregard them and confine ourselves to comparison of materials at corresponding stages of elongation—and in which, for the present, only "frozen in" states are considered.

MATERIALS

Previously, it was found that only colloids containing autonomic hydroxyl, or perhaps an equivalent amino-group, as in proteins, were reactive. It was further observed that polyvinyl alcohol was reactive independently of moisture content, within measurable limits. At this stage, therefore, attention was largely concentrated on materials of the two macromolecular series:

1. Polyvinyl acetate \leftrightarrow polyvinyl alcohol.
2. Cellulose triacetate \leftrightarrow cellulose.

INFLUENCE OF ADSORBED WATER (MOISTURE REGAIN)

Neither fully acetylated polyvinyl acetate, nor "cellulose triacetate," shows more than a trace of

response at any humidity. Very slight residual effects at high humidity might be due to "spots" of incomplete esterification. With polyvinyl acetate there is practically no effect of moisture at either extreme of composition, but there is a definite sensitivity for intermediate, partly acetylated or deacetylated materials (cf. Fig. 3). With cellulose, while there is practically no effect of water upon the "triacetate," there is a steadily increasing effect on deacetylating, no maximum being reached, but the greatest effect occurring with cellulose itself (cf. Fig. 4).

Actually, the range of water adsorption—in terms of vapor pressure or relative humidity—which could be studied was limited by the rigidity of the sample. Above a certain value the disk becomes flabby and badly distorted. Even before this, the adsorption of water tends to a deformation, and there occurs swelling and dilation principally transverse to the direction of stretch, as shown in previous studies on gelatin.¹ The over-all behavior is therefore represented by that shown in Fig. 5 (for gelatin). The transverse expansion introduces a "form" anisotropy which first counteracts and then surpasses the internal anisotropy.

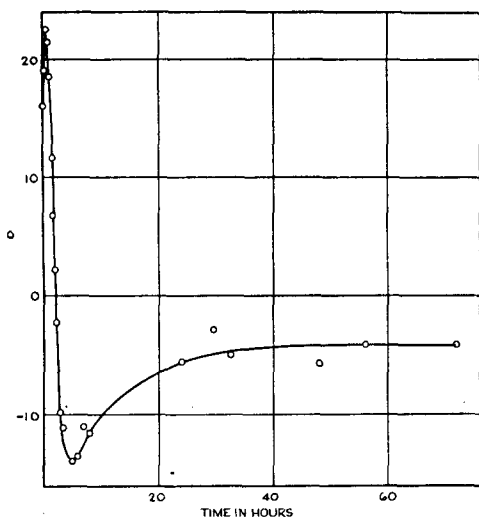


FIG. 5. Change of E. A. of gelatin with time at 95 percent R. H. due to unequal swelling along and across direction of elongation. Note: The open circle shown to the left of the above figure should be ϕ .

¹ S. E. Sheppard and J. G. McNally, *Colloid Symposium Annual* (John Wiley & Sons Inc., New York, 1930), Vol. VII, p. 17.

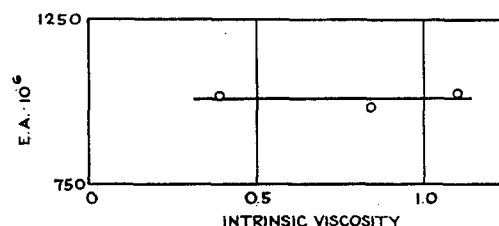


FIG. 6. Relation of E. A. to intrinsic viscosity (chain length) of polyvinyl alcohol samples.

EFFECT OF MOLECULAR WEIGHT OR CHAIN LENGTH

A number of polyvinyl alcohol samples having, according to measurements of their specific viscosities, considerably different average molecular weights, was examined. It appeared (cf. Fig. 6) that the E. A. is independent of the mean molecular weight and chain length, at any rate over a considerable range.

CORRELATION OF ELECTRICAL ANISOTROPY WITH OPTICAL BIREFRINGENCE

In Part I definite birefringence measurements were adduced as evidence of "fibering," of macromolecular orientation, for the sheets examined. This relation has been studied in greater detail.

As noted, with increasing elongation, the E. A. of polyvinyl alcohol increases regularly—and approximately linearly—up to about 250 percent, when the rate of increase of E. A. appears to decrease rather sharply (cf. Fig. 2). The optical birefringence was also observed to increase at first linearly with the elongation, but then a nonlinear region, with indications of approach to a limit, supervened (cf. Fig. 7). For the primary linear relation between the E. A. and the optical birefringence for the same material, see Fig. 8.

What has just been said applies only to the hydrophile colloids which manifest the property of electrical anisotropy, and not to the purely organophile ones, such as cellulose triacetate, or polyvinyl chloride which become birefringent on elongation, but not electrically anisotropic. Moreover, while in most cases the optical birefringence is *positive*, in the sense that $n_\gamma > n_\beta$, where the maximum index n_γ is in the direction of the elongation, this is not necessarily the case. Examples were noted in Part I where n_γ could be perpendicular to the plane of the sheet, and

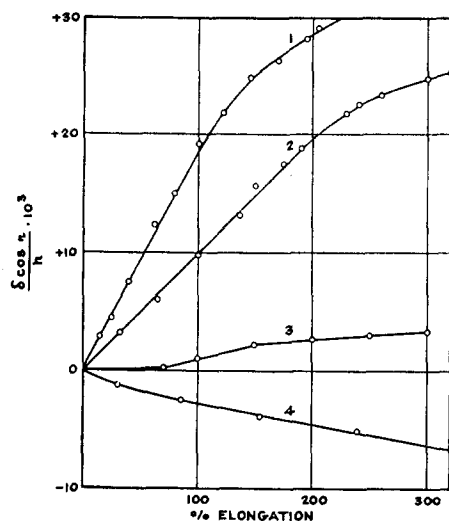


FIG. 7. Influence of elongation on the birefringence of polyvinyl alcohol and polyvinyl acetates. 1. Polyvinyl alcohol. 2. Hydrolyzed polyvinyl acetate (73 percent polyvinyl alcohol). 3. Hydrolyzed polyvinyl acetate (35 percent polyvinyl alcohol). 4. Polyvinyl acetate.

it could happen that it would be in the plane of the sheet, but approaching a perpendicular direction to the axis of stretch. Such conditions occur, with higher alkyl esters of cellulose² and with polyvinyl acetate, when alignment of optical density, by side chains, may be greater transverse to the backbone spacings of the chain molecules. With partly hydrolyzed polyvinyl acetate, the optical birefringence $n_\gamma - n_\delta$ decreases with decreasing —OH content from positive to negative, going through a zero value at about 6 percent hydroxyl (cf. Fig. 9).

DISCUSSION

The change from a well-marked *linear* relation (over a considerable range) to a non-linear one may well indicate something like a phase transition, such as occurs in the "crystallization" of rubber upon high elongation.³ In the case of polyvinyl alcohol, a sample at some 250 percent elongation gave such a well-marked fiber pattern (cf. Fig. 10) as to indicate that something of the sort is occurring, and this will be followed up by further x-ray diffraction observations.

In the previous paper it was suggested that the phenomena observed might be accounted for by

² J. Spence, J. Phys. Chem. **43**, 865 (1939); **45**, 401 (1941).

³ H. Mark, Ind. Eng. Chem. **34**, 1343 (1942).

the formation of oriented chains of hydrogen bonds, relatively rigidly connected with, or integrated in, the long-chain structure of the colloid macromolecules. The outstanding effects which have to be explained are:

1. Absence of effect with purely organophile (hydrophobe) colloids (polymers). It appears that Wood's interpretation in terms of a differential dielectric capacity along and across an axis of fibering, while a relevant, and, in a sense, obligatory concomitant, is not a sufficient cause.

2. It is thought that the role of effective —OH groups, whether derived from constitutional hydroxyls (and perhaps amino- or imino-groups in proteins) or from these reinforced by adsorbed water molecules, is to form quasi-electronically conducting chains.

In the case of polyvinyl alcohol an idealized image of a parallel group of such chains, part of the molecules, is shown in Fig. 11.

In the dry material it is supposed that the chain molecules are aligned, side by side, with alternate hydrophobe (—CH₂) and hydrophile —OH adjacent alignment.[†] The extreme ease of lengthwise splitting supports this view.

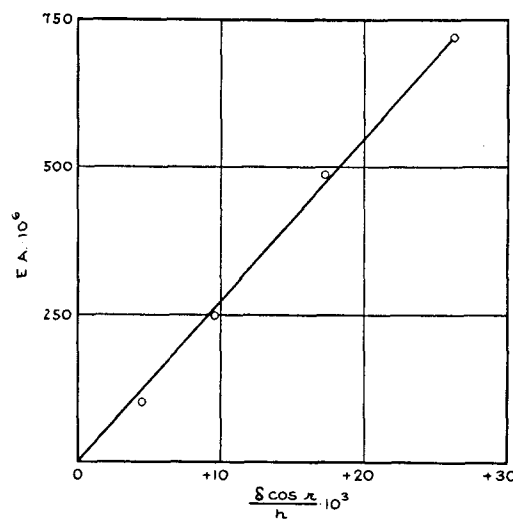


FIG. 8. Relation between electrical anisotropy and optical birefringence of polyvinyl alcohol.

A recent x-ray study of the structure of (crystalline) polyvinyl alcohol⁴ indicates that some modification of this picture may be neces-

[†] *En bloc*, as compared with a plane, some complications of the arrangement might occur.

⁴ Rose C. L. Mooney, J. Am. Chem. Soc. **63**, 2828 (1941).

sary, at any rate for well-crystallized material. It was not stated how the material was prepared but merely that "well-oriented samples can be obtained, the fiber periodicity is short, and the chemical composition known and simple." The structure concluded to represent the observations best did not accord with the assumption just made that the hydrogens are lying (as bridges) between successive oxygens in the same plane. This would not explain the 2.72Å separation between oxygens of adjacent chains, and would give "a hydrogen bond distance somewhat shorter than is usual in alcohols. A more reason-

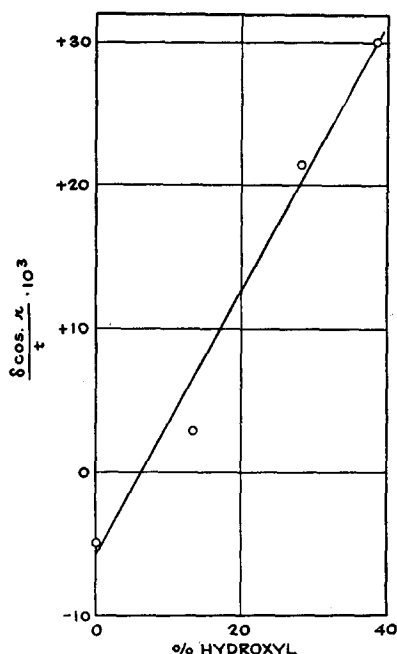


FIG. 9. Effect of hydroxyl content on the optical birefringence of hydrolyzed polyvinyl acetates at 225 percent elongation.

able arrangement is that illustrated in Fig. 2 [our Fig. 12]. This shows *paired* vinyl alcohol chains projected in the 101 plane. The structure, as deduced from x-ray diffraction, is considered to consist of pairs of long-chain molecules, held together by hydrogen bonds. These double chains all lie along the fiber axis, but in random orientation about it. . . . Each chain has a zigzag carbon planar configuration, with glycol units in the 1, 3 position."

It appears that this paired structure would still permit of continuous hydrogen-bond chains.

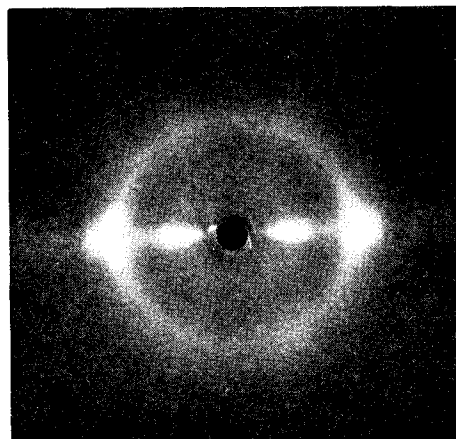
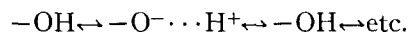


FIG. 10. Diffraction diagram, Cu $K\alpha$ of polyvinyl alcohol at 250 percent elongation, parallel to plane of sheet and perpendicular to direction of elongation.

The ease of splitting longitudinally observed in our specimens would still be possible, provided the double chains were not in too random orientation about the fiber axis. Also it is possible, as already mentioned, that crystallization occurs rather abruptly as a function of elongation and orientation. Insofar as H-bonding and conductance are concerned, the two molecular chains constitute only one shared H-bond chain.

A kind of electronic conduction could take place along the macromolecular chain by way of a quantum molecular resonance process; the hydroxyl can be regarded as resonating between the states symbolized below:



In an electric field a torque would be produced proportional to V^2 , to the total current capacity of the conductors, and to $\sin \theta \cos \theta$ ($\propto \sin 2\theta$),

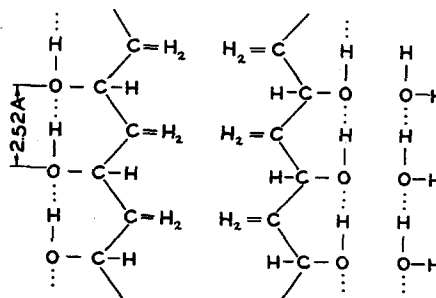


FIG. 11. Formation of chains of hydrogen bonds in polyvinyl alcohol (adsorbed water may form a separate chain as shown).

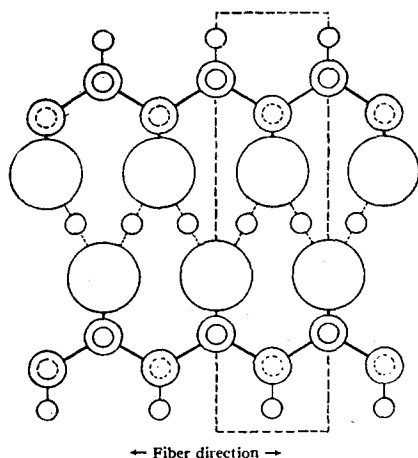


FIG. 12. [From Rose C. L. Mooney, J. Am. Chem. Soc. 63, 2828 (1941).] Polyvinyl alcohol chains projected on the 101 plane. The circles, in descending order of size, represent oxygen, carbon, and hydrogen. The dotted and solid circles distinguish between hydrogens on alternate sides of the chains.

where θ is the angle between the axis of the conductor, and that of the electric field. The "independence of length" for polyvinyl alcohol, etc., seems somewhat at variance with the effect of adsorbed water with partly hydrolyzed polyvinyl acetates. In this case, evidently *gaps* would exist in the molecular chains, consisting of residual acetyl groups. It appears that these can be "bridged" by adsorbed water molecules. Beyond a certain composition, the nearer this latter approaches 100 percent polyvinyl alcohol, the less effective are the additional water molecules.

Considering again a completely stretched cellulose macromolecule or chain, then according to x-ray and other indications⁵ it appears that while the two secondary —OH groups in one glucosan unit can possibly supply an H bond between themselves, it would be quite difficult for a primary —OH of one glucosan to bridge to a secondary —OH of a contiguous glucosan. Only by adsorption of water molecules could the two chains of H bonds be formed, as compared with the *one* chain feasible for polyvinyl acetates (cf. Fig. 13). This seems a reasonable explanation why the E. A. of partly hydrolyzed polyvinyl acetates increases linearly at first with the

⁵ K. H. Meyer and H. Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe* (Akad. Verlagsges. m.b.H., Leipzig, 1930).

density of adsorbed water molecules, while with cellulose a power (initially 2) of the adsorption density seems involved. Exact relations are improbable, particularly for cellulose, because thermal and other conditions would affect the strength of individual hydrogen bridges, or, conversely, the interval necessary. Certainly for resonance and conductance along the chain, the strength of the H bond would have to be limited possibly up to 2.9 Å.⁶ This could be satisfied readily enough in polyvinyl alcohol itself and probably without much difficulty in the "gaps" for hydrolyzed polyvinyl acetates, but in cellulose both the stereochemical and the energetic

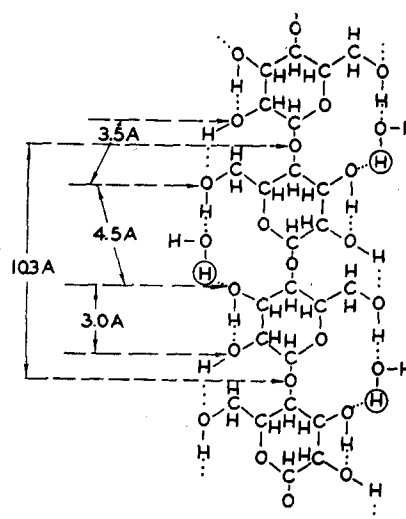


FIG. 13. Continuous hydrogen bonding in cellulose by the addition of one mole of water per glucose residue (bonds contributed by water are indicated by circles).

conditions for the adsorption are considerably more complicated. The figure given (Fig. 13) is based on the configuration deduced in the paper of Meyer and Misch⁷ of 1937. In a recent paper by P. H. Hermans, J. de Booy, and C. J. Maan⁸ certain modifications are suggested, which are of importance in regard to the regain of moisture (water adsorption) and to the bearing of this upon electrical anisotropy. These changes are

⁶ L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, New York, 1940), second edition, p. 289.

⁷ K. H. Meyer and L. Misch, *Helv. Chim. Acta* 20, 232 (1937).

⁸ P. H. Hermans, J. de Booy, and C. J. Maan, *Kolloid Zeits.* 102, 169 (1943).

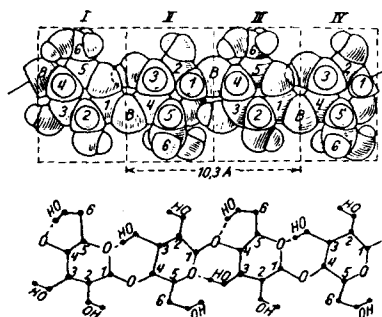


FIG. 14. [From P. H. Hermans, J. de Booy, and C. J. Maan, *Kolloid Zeits.* 102, 177 (1943).] (a) Stuart model of the cellulose chain with spatial puckering viewed from above (oxygen atoms shaded). (b) Diagram of the corresponding nuclear structure.

largely based upon a remodelling using van der Waals radii (according to Stuart) for the atoms, and instead of a planar pyranose (hexose) ring, a puckered one, according with the "armchair" form of the cyclohexane ring.

In Fig. 14 is shown their "most probable configuration of the straight, stretched cellulose molecule with spatial buckling, and using Stuart's atom-models (van der Waals radii) viewed from above. It will be seen that the bridge oxygen between nuclei II and III lies somewhat downward, and, between I and II, or equally III and IV, somewhat upward [of a median plane] while the horizontal buckling factor is clearly evident. The model also shows that a horizontal buckling in the opposite sense would lead to steric hindrance." *

"Herewith only the choice of position of the $-\text{CH}_2\text{OH}$ groups is left free. In Fig. 12 these [groups] are placed alternately in the 'normal' and the 'reverse' positions. $-\text{OH}$ group 3 is given a particular position with respect to the ring-oxygen atom of the adjacent ring, such as to give a hydrogen bond. Likewise, such an H-bond is possible between the $-\text{OH}$ in normal position at C-atom 6, and the glucosidic bridge-oxygen. By these additional ring systems, the stretched position of the chain might be further strengthened, since rotation about the glucoside bridges would be hindered."

The authors also point out this notable peculiarity of the β -glucose configuration [as adopted, cf. Figs. 2 and 3 of their article]. "All the hy-

droxyl groups find themselves on the side of the ring extension, while above and below only hydrogen-carrying valences project. The cellulose chain has actually a somewhat flattened shape and *therewith two [2] hydrophobe and two [2] hydrophile sides.*[†] With no other hexose than β -glucose can such a relation be obtained.

It is apparent that the configuration suggested by these authors would involve somewhat different conditions for the adsorption of water vapor, and for its effect upon electrical anisotropy, from those deducible from the earlier Meyer-Mark chain macromolecule. However, evidently in one important respect they are alike, *viz.*, in predicating a duplex or twofold array of adsorption "sites" for water to form continuous H-bond chains. The temperature coefficient of adsorption, or, more precisely, the differential adsorption heat, would seem likely to be of different magnitude and trend for the two cases, and may help to decide between them. The newer model, especially if the preferred formation of H bridges between glucosan $-\text{OH}$ groups and bridge oxygens be accepted, would appear to require longer chains of oriented adsorbed water molecules than the earlier one.

We may note in this connection that S. Baxter⁹ has suggested that the electrical conduction of textile fibers, e.g., wool, involves a mechanism other than electrolytic. He suggests an electronic conduction, as in a semiconductor. It is assumed that "the dry wool fiber is an almost perfect insulator, and that adsorbed water molecules cause 'impurity centers' giving rise to electronic conduction." We are not convinced, for reasons which will be discussed elsewhere,** that much of the direct (macro) conductance is not electrolytic, but agree in part with Baxter for an inner, residual electronic portion. The actual mechanism of this we consider to be by way of a hydrogen-bond resonance process, as indicated here.

A study of the temperature coefficients is contemplated, as well as of other factors, in the relation of electrical anisotropy to electrical conductance.

[†] Our italics.

⁹ S. Baxter, *Trans. Faraday Soc.* 39, 207 (1943).

** In connection with the conductance of gelatin.

* Between hydrogens of successive glucosans.