Electrical Anisotropy of Xerogels of Hydrophile Colloids Part I

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Electrical Anisotropy of Xerogels of Hydrophile Colloids

Part I*

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A number of colloid materials—proteins, plastics, and the like—have been coated in sheet form and "fibered" internally by stretching to 100 percent or more elongation. Circular disks were cut from the fibered sheets, and their degree of orientation measured in an (alternating) electric field. Account is given of the relation of the orientation measured to field strength, thickness, humidity, and moisture content. It was observed that induced electrical anisotropy is not shown by all kinds of natural and synthetic colloids; thus it is not shown by organophile xerogels, but only by the hydrophile ones. With most of these the electrical response depends upon the relative humidity and the absorbed water content, but with polyvinyl alcohol the effect was independent of the absorbed water.

INTRODUCTION

IT is well known that elongated particles in an electric field, if free to rotate, become oriented with their long axes parallel to the electric force. H. J. Woods[1] observed that wool cells exhibit the effect in high degree, being about 100μ in length, and only a few microns thick. When suspended in water they are readily pulled into alignment by an alternating field—used in place of a direct field to prevent drift of the cells.

Woods made the further observation that *circular* pieces, cylinders, or disks, of finger nail and of cow's horn, when suspended horizontally by a silk thread in an alternating field, tended to orient so that the direction of the protein chain was parallel to the electric force. Randomly oriented films of myosin and of denatured proteins showed no such electrical anistropy unless previously stretched. Such orientation was explained as due to a difference of dielectric constant for fields parallel and perpendicular, respectively, to the protein chains. However, the orienting effect caused by internal anisotropy was much less than that dependent on external shape. If the eccentricity exceeded about 0.4, the effect of fiber orientation could no longer be detected.

It appeared to us that the electrical orientation of disks might furnish interesting information on the direction and extent of molecular or micellar orientation, and we decided to apply it to various proteins, cellulose derivatives, and synthetic resins. Conversely, it appeared possible, from previous observations[2] on the influence of molecular or micellar orientation in cellulosic films upon static electrification, that the production of temporary electrets might throw light upon this problem also.

APPARATUS AND OPERATIONS

The sheet material was usually prepared in the form of disks 1.50 cm in diameter, but in some cases (for investigating the form factor) as oblong rectangles 1.50 cm long and 0.25 cm wide. In measurements they were suspended from a torsion head by a pure nickel wire 50.5 cm long and 0.00432 cm in diameter (cf. Fig. 1). The specimens were not attached directly to the wire, but to an intermediate short length of glass rod surmounted by a mirror 0.5 cm square which, in turn, was cemented to the wire. The section of glass rod prevents arcing between the electrodes and the wire. The electrodes consisted of pieces of brass rod 1.905 cm in diameter mounted 2 cm apart in Bakelite blocks. The image of a single-wire filament lamp was reflected from the small mirror and focused on the circular scale to permit measurement of the electric orientation. The measurement consisted in determining the

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[1] H. J. Woods, Proc. Roy. Soc. London **A166**, 76 (1938).

[2] Unpublished observations of J. G. McNally of these Laboratories.

rotation of the torsion head necessary to bring the image of the lamp filament back to its zero position prior to application of the electric field.

The entire suspension, excluding the torsion head itself, was enclosed in a glass case firmly closed in front by a glass door. This eliminated disturbance by air currents and allowed control of humidity and temperature. The torsion wire extended through a very small hole drilled in the top of the enclosure.

RELEVANT QUANTITATIVE FACTORS

The voltage applied could be varied from 0 to 25,000 volts a.c. by the use of a transformer and a Variac (General Radio Company). The couple G required to twist the wire through an angle ϕ is given by the equation

$$G = na^4\phi/2l, \tag{1}$$

where a = radius of wire in cm, l = length of wire in cm, and n = rigidity of wire in dynes per cm². The rigidity n was determined by measuring the period of oscillation of a thin brass disk having about the same weight as that of the suspended system actually used, viz., 0.6 gram, and attached to the end of the wire. The value obtained was 6.44×10^{11} dynes per cm², whence the calculated value of G is 0.439 dyne per radian.
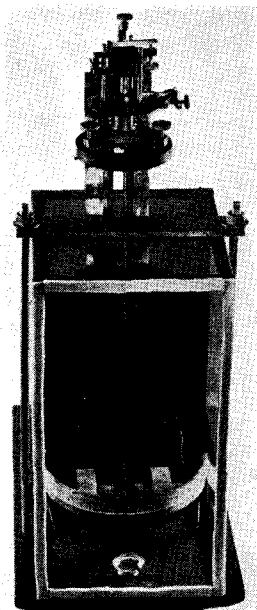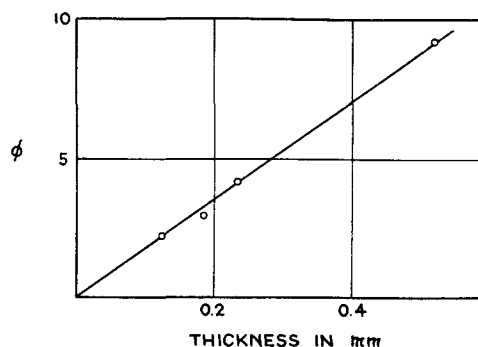
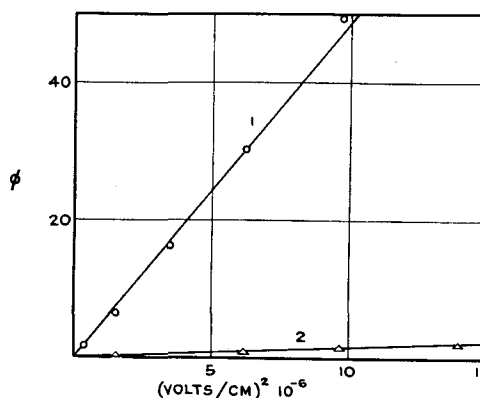FIG. 2. Effect of thickness of specimen (cellulose acetate, 40 percent acetyl) on electrical anisotropy.

FIG. 3. Relation of E. A. to applied potential for polyvinyl alcohol and a polyvinyl (butal) (Vinylite X).

The electrical anisotropy, measured as ϕ, the angle of rotation, is expressible in reduced measure per unit volume as follows: It is a volume or mass property, proportional, therefore, to the thickness t of the specimen, as shown in Fig. 2. Further, the flux density of electrification will be proportional to V^2, where V is the applied potential difference between the electrodes,[3] experimentally demonstrated in Fig. 3. With circular, i.e., cylindrical reactors, there would be no electrical response for isotropic material. Otherwise, we have an axis of anisotropy, and the electrical response will be a function of the angle θ between this axis and that of the applied field. Functionally, then, ϕ is proportional to $\sin \theta \cos \theta$, that is, to $\sin 2\theta$. By setting θ at 45°, this factor becomes unity, and may be omitted. In our case, the *anisotropy* was enforced by

[3] Cf. J. S. Donal, Jr., and D. B. Langmuir, Proc. I. R. E. **31**, 208 (1943).

TABLE I. Electrical anisotropy of various colloids in disk form.

Material	Percent water absorption at 50% R. H.	Percent elongation	Hydroxyl content percent	E. A. ϕ/V^2t at 50% R. H.	Bire-fringence $n_\gamma - n_\beta$	X-ray evidence of orientation
Polyvinyl alcohol	6.7	250	38.6	$195 \cdot 10^{-6}$	$2350 \cdot 10^{-5}$	Yes
Gelatin	16.0	200		141	293	Yes
Cellulose acetate, 24.5% acetyl	8.1	100	14.8	23	1200	Yes
Polyvinyl acetal	3.8	350	6.4	10	544	Yes
Hydrolyzed polyvinyl acetate	2.5	550	5.5	9	12*	No
Vinylite X	1.9	220	9.1**	8	1120	Yes
Cellulose acetate, 40% acetyl	3.5	100	3.2	0	460	Yes
Cellulose nitrate	1.5	100	4.7	0	364	Yes
Polyvinyl acetate, R. H. 361	1.0	250	0	0	2*	No
Polyvinyl acetal	2.4	250	3.0	0	1250	Yes
Polystyrene	0.03	300	0	0	12*	No

* Maximum index n_γ is perpendicular to plane of the sheet in these cases. See J. Spence, J. Phys. Chem. 43, 865 (1939); 45, 401 (1941).
** Calculated on the assumption of one hydroxyl group to one divinylbutal group.
Note: Dependence of E. A. and the electrical conductance on water content is noted in the text.

stretching the original samples; on cutting out circular disks, the axis of anisotropy was parallel to the direction of (pre-)stretching. This conclusion, and the presence of anisotropy produced by stretching were confirmed by measurement of the optical birefringence (for material sufficiently transparent) and by x-ray diffraction investigation. Confirmation of the $\phi \propto \sin 2\theta$ relation is afforded by the results shown in Fig. 4. In our experiments, however, θ was generally set at 45°, when $\sin 2\theta = 1$ and does not appear in the expression.

OPERATING CONTROLS

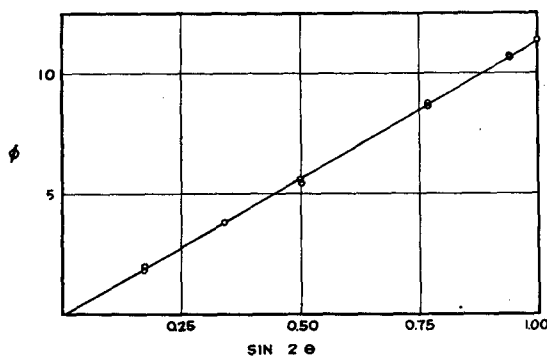The materials tested (cf. Table I) were usually coated from solution in sheet form on glass, and

FIG. 4. Relation of E. A. to $\sin 2\theta$.

after drying and stripping were stretched under conditions giving high internal orientation, as indicated by birefringence, x-ray diffraction, and practically complete elastic recovery at or near

the initial (high) temperature and contents of water and solvent. Certain particulars of this are discussed later.

Relative humidity inside the apparatus chamber was adjusted by solutions of sulfuric acid of suitable concentration.[4] Measurements of electrical conductivity of certain materials were made by the procedure described by Sheppard, Houck, and Dittmar.[5] Measurements of optical birefringence and examination of x-ray diffraction were made on practically all of the sheet materials.

EXPERIMENTAL RESULTS

The relative magnitude of the electrical anisotropy can be expressed by the quantity ϕ/V^2t (disposing of θ as previously noticed). A more explicit measure, involving the torque or couple G corresponding to the angle ϕ [cf. Eq. (1)] in dynes per radian, and other factors is under consideration.

Table I lists a number of materials in descending order of the relative E. A. Also given are such factors as the percentage elongation, the hydroxyl content of the molecule, where known, the actual water content at 50 percent relative humidity, etc.

It is apparent from the table that the property of induced electrical anisotropy—induced by stretching—is not shown by all kinds of natural and synthetic colloids, but is limited (a) to

[4] R. E. Wilson, Ind. Eng. Chem. 13, 326 (1921).
[5] S. E. Sheppard, R. C. Houck, and C. Dittmar, J. Phys. Chem. 44, 185 (1940).
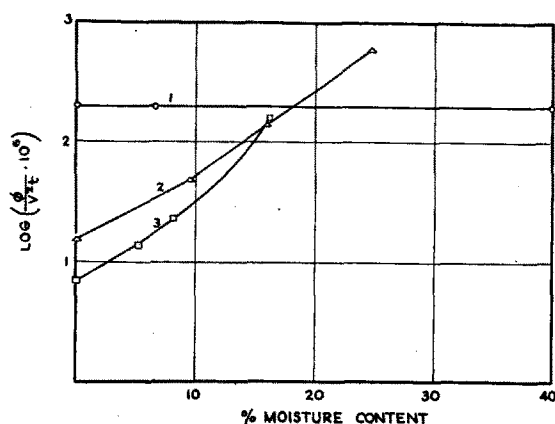
FIG. 5. Relation of E. A. to moisture content for: 1. Polyvinyl alcohol, 2. Gelatin, 3. Cellulose acetate (24.5 percent acetyl).

those containing an appreciable amount of fixed hydroxyl and/or absorbed water, and (b) those capable of absorbing considerable water. A further differentiation is noted in Table II and Fig. 5.

TABLE II. Dependence of electrical anisotropy and conductivity on water adsorption.

Material	Electrical anisotropy	Electrical conductivity
Polyvinyl alcohol	No	Yes
Gelatin	Yes	Yes
Cellulose acetate, 24.5% acetyl	Yes	Yes

INFLUENCE OF HUMIDITY AND ABSORBED WATER

It will be seen that whereas with gelatin and hydrolyzed cellulose acetate, the E. A. varies sharply with absorbed water content, in the case of *polyvinyl alcohol* it is independent of the water content, although this material strongly absorbs water—becoming indeed soluble therein.

Although the E. A. of polyvinyl alcohol is independent of absorbed water, its electrical conductance is dependent. Within certain limits, the logarithm of the conductance is a linear function of the logarithm of the water content (cf. Fig. 6). It had been previously observed by Sheppard, Houck, and Dittmar[5] that the logarithm of the conductance of gelatin is directly proportional to the water content. Combining this result with present observations, we find that the logarithm of the E. A. for gelatin varies linearly with the logarithm of the conductance (cf. Fig. 7).
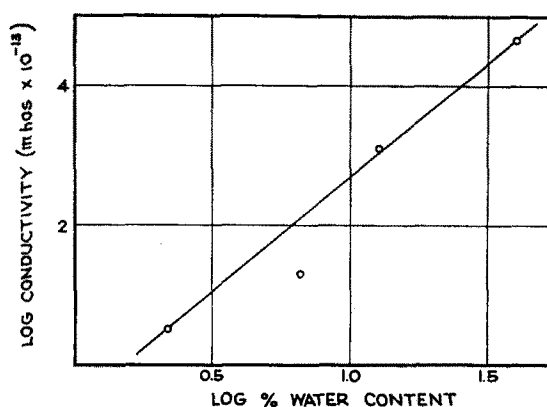

FIG. 6. Relation of conductance of polyvinyl alcohol to water content.

DISCUSSION

One principal result from this survey is that electrical anisotropy in colloids as xerogels[6] is limited to hydrophile or hydroxylated substances, which further have an axis of physical (structural) anisotropy. It is not solely a matter of an (induced) structural anisotropy (with varying dielectric capacity along and across) as suggested by Woods.[1] This is shown by the inactivity of the hydrophobe colloids, such as vinylite, polyvinyl acetate, etc.

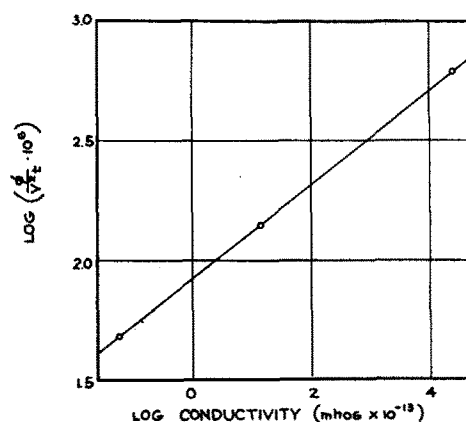A further notable result is the contrast be-

FIG. 7. Relation of log (E. A.) to long conductivity with gelatin.

tween polyvinyl alcohol, on the one hand, and the hydrophile cellulose acetate and gelatin (and presumably cellulose and proteins in general).

[6] Term used for dried colloid gels. Cf. S. E. Sheppard, Trans. Faraday Soc. 29, 77 (1933).

Whereas the former shows electrical anisotropy independent of moisture content (although hygroscopic), the latter are only electrically anisotropic on taking up water, and increase proportionately. This indicates a preponderant role of −OH groups—in the case of polyvinyl alcohol, a preemptive role of the structural hydroxyls, which in the cellulosic and protein bodies, can be assumed by adsorbed water.

It appears probable that the phenomenon is connected with the formation of oriented −OH or H-bridge chains. However, certain questions persist, e.g., why the −OH groups of cellulose cannot function *per se* but require adsorbed water. This may be a matter of spacing or contiguity. Next, why the effect with polyvinyl alcohol does not increase with adsorption of water. Perhaps this indicates a species of "saturation" already achieved by the molecular hydroxyls. Before more explicit answers can be given, or a definite mechanism be proposed, it is desirable that more and fuller data be obtained. We are examining *amylose*[7] and various protein substances, as well as specific modifications of polyvinyl alcohol and polyamides, and will report on these later. From the further experiments now planned it should be possible to indicate the mechanism of E. A. more clearly, and to relate it to the structure of these colloids.

ACKNOWLEDGMENT

[7] R. E. Rundle, L. Daasch, and D. French, J. Am. Chem. Soc. **66**, 130 (1944).