

are therefore in absolute value  $\leq \frac{knNK}{\frac{1}{2}T} = M$ , so that the point with these coordinates belongs to  $\mathfrak{B}$ . This set, containing the  $k-1$  points with the coordinates (19), contains also the point with the coordinates  $\{1 + T J^m(l_0)\} \psi(l_0) P_v$ , where  $P_v$  is defined by (14), so that it contains moreover the point with the coordinates

$$(1 - \lambda) \{1 + T J^m(l_0)\} \psi(l_0) P_v + \lambda \frac{Q_v(l_0) - P_v}{\frac{1}{2} T J^m(l_0)} \psi(l_0) = \zeta Q_v(l_0),$$

where

$$\begin{aligned} \zeta &= (1 - \lambda) \{1 + T J^m(l_0)\} \psi(l_0) = \frac{\lambda}{\frac{1}{2} T J^m(l_0)} \psi(l_0) \\ &= \frac{1 + T J^m(l_0)}{1 + \frac{1}{2} T J^m(l_0) + \frac{1}{2} T^2 J^{2m}(l_0)} \psi(l_0) > \psi(l_0), \end{aligned}$$

if  $J(l_0)$  is small enough, that is, if  $(l_0)$  lies near enough to the origin.

In this manner we obtain a contradiction and we find that there exists a positive number  $p$  such that to any point  $(l_0)$  of  $\mathfrak{L}$  with  $\sum_v |Q_v(l_0)| > 0$  and  $J(l_0) \leq p$  corresponds one  $\mu$  at least ( $1 \leq \mu \leq k-1$ ) with the property that the point with the  $n$  coordinates (19) does not belong to  $\mathfrak{B}$ . If more than one such value of  $\mu$  is possible, I choose the smallest value with this property; I put  $l_{\mu_0}(x_r) = l'_0$ . The point with the  $n$  coordinates  $\{1 + T J^m(l_0)\} \psi(l_0) Q_v(l'_0)$  does not belong to  $\mathfrak{B}$ , so that

$$\sum_v |Q_v(l'_0)| > 0 \quad \text{and} \quad \psi(l'_0) \leq \{1 + T J^m(l_0)\} \psi(l_0);$$

from the condition (4) it follows that

$$J(l'_0) \leq \vartheta J(l_0) \leq \vartheta p$$

In the same manner we find a point  $(l''_0)$  of  $\mathfrak{L}$  satisfying the inequalities

$$\psi(l''_0) \leq \{1 + T J^m(l'_0)\} \psi(l'_0) \quad \text{and} \quad J(l''_0) \leq \vartheta^2 p,$$

and so on. Thus we obtain an infinity of points  $(l^*_0)$ , all belonging to  $\mathfrak{L}$ , such that

$$J(l^*_0) \rightarrow 0 \quad \text{and} \quad \psi(l^*_0) \leq (1 + T \vartheta^{mh} p^m) \psi(l^*_0),$$

and therefore

$$\psi(l^*_0) \leq \psi(l_0) \prod_{h=0}^{\infty} (1 + T \vartheta^{mh} p^m) \quad \dots \quad (20)$$

$J(l^*_0) \rightarrow 0$  implies that  $(l^*_0)$  approaches the origin  $l_0 = 0$ , so that it follows from (7) that the point with the  $n$  coordinates  $Q_v(l^*_0)$  approaches the origin  $x_r = 0$ . Hence  $\psi(l^*_0)$  increases indefinitely, contradictory to (20). This proves the theorem.

(To be continued.)

Medicine. — Spreading of gliadin. II. By E. GORTER and P. C. BLOKKER.

(Communicated at the meeting of February 28, 1942.)

The measurement of the changes in surface potential was made using YAMINS and ZISMAN's method<sup>1)</sup>. A gold plate, placed close above the surface of the liquid is made to vibrate. Plate and liquid together form a condenser which is connected with the grid circuit of a valve detector. The alternating current generated is amplified and is made audible with a telephone; when the potential difference between liquid and gold plate is compensated by means of a potentiometer, the sound in the telephone reaches a minimum. The gold plate was set vibrating with an electrically driven tuning-fork instead of with the loudspeaker vibrator used by the authors mentioned, as with the first method we got less difficulties in screening the vibration source. The vibration amplitude was made very small so as to prevent the surface of the liquid coming into vibration too much. To amplify the alternating current produced we used a three set amplifier. The first tube was a Philips E 446, a tube with a very high amplifying factor. The limits of error of the measurements were  $\pm 1$  mV., the duplicability, however, was much less.

The viscosity measurements were made with a torsion pendulum<sup>2) 3)</sup> which method is the most suitable for films with rather high viscosities. As rotating body a massive gilt brass cylinder (27 mm diam.) was used, as torsion wire a very thin phosphorbronze wire (50 cm length). With a lense and a mirror fixed on top of the cylinder just beneath the point of attachment of the wire, the image of an illuminated arrow was formed on a circular scale (1 m diam.) The moment of inertia of the system was 230 g cm<sup>2</sup>, the torsion constant of the wire 86 g cm<sup>2</sup> sec<sup>-2</sup>, the period of oscillation 10.4 sec. At viscosities lower than about 8 g sec<sup>-1</sup> the logarithmic decrement of the oscillations was measured; above viscosities of about 200 g sec<sup>-1</sup> the motion was aperiodic so that the decrease of the amplitude with time could be measured; in the region between these viscosities no measurements were made. With a paraffined glass rod placed across the spreading through a square with an edge of 14 cm was obtained, the glass rod, the two long edges of the trough and the piston of the differential balance being the border.

#### Surface potentials for gliadin and gliadin-tannic acid films.

In fig. 4 the difference in surface potential for buffers with and without films upon it ( $\Delta V$ ) is plotted against the surface concentration at different pH values. In doing so one gets an idea of the concentration and orientation of the molecules in the surface, for it may be expected that  $\Delta V$  increases almost proportionately to the number of molecules present in the surface when the orientation does not change and the molecules only little influence each other.

Under a pressure of 0.5—1 dn/cm the potential was very inconstant, which points to the film being inhomogeneous. Above this pressure the variations in surface potential were within the limit of error of the measurements ( $\pm 1$  mV), except in the region of 7 dn/cm and higher in some cases. In these cases, moreover, the minimum in the telephone was not sharp, which, according to YAMINS and ZISMAN<sup>1)</sup> points to the presence of inhomogenities in the film. Sometimes the potential was even 50 m.V. under the normal values over a considerable pressure range. Then at higher pressures the potential increased rather rapidly, so that in the region where  $\Delta V$  only slightly changed

<sup>1)</sup> H. G. YAMINS and W. A. ZISMAN, J. chem. Physics, 1, 656 (1933).

<sup>2)</sup> I. LANGMUIR, J. Am. chem. Soc. 59, II, 2410 (1937).

<sup>3)</sup> M. JOLY, J. chim. Phys. 36, 285 (1939). Kolloid Z. 89, 26 (1939).

with the concentration, the reproducibility was always good. These phenomena are presumably caused by the transition from the liquid to the gelatinous state already mentioned in our first article.

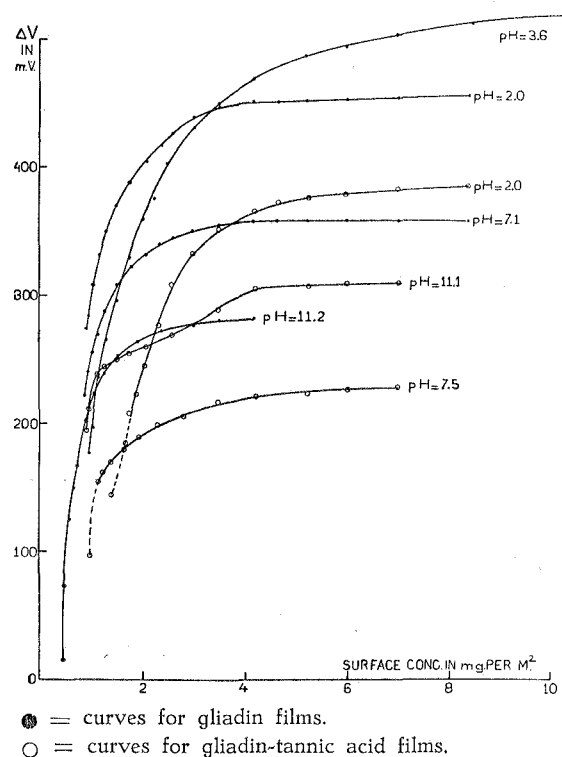


Fig. 4. Surface potential differences of gliadin and gliadin-tannic acid films, as a function of the surface concentration.

The curves show that at the lower concentrations  $\Delta V$  increases rapidly and almost proportionately with the concentration, which indicates a practically constant „dipole moment”; in this region presumably free water molecules are squeezed out of the spaces in and between the micellae. At higher concentrations the increase of  $\Delta V$  becomes smaller and smaller. COCKBAIN and SCHULMAN<sup>4)</sup> have made it very comprehensible that in this region the orientation of the polypeptide chains changes. It is also possible, however, that hydration water (bound to the polar groups of the gliadin) is pressed out of the film as seems to be the case, according to LANGMUIR, with films of fatty acids; this would also cause a decrease of the  $\Delta V$  increase (see PHILIPPI<sup>5)</sup>). At very high surface concentrations  $\Delta V$  finally becomes practically constant, probably because the closest packing is obtained and gliadin molecules are pressed out of the film on further compression. In full agreement with this is the fact that the constant  $\Delta V$  values always occur at a pressure of about 20 dn/cm, the same pressure at which the compressibility strongly increases and the pressure falls rapidly after each compression. In the case of gliadin-tannic acid films the constant  $\Delta V$  values occur at pressures above 30 dn/cm (see also fig. 1 and 4). This latter observation is a strong indication that the decrease

4) E. G. COCKBAIN and J. H. SCHULMAN, *Trans. Faraday Soc.* **35**, 1266 (1939).

5) G. TH. PHILIPPI, *On the nature of proteins*. Thesis Leyden 1936.

in pressure after compression above 1 dn/cm has not to be considered as collapsing of the film, but that this occurs only at pressures above 30–40 dn/cm.

In fig. 5 the well reproducible final  $\Delta V$  values are plotted against the pH. This figure shows that in the case of gliadin at low pH values  $\Delta V$  is very great and passes a maximum; at higher pH values  $\Delta V$  decreases rather rapidly. For the explanation of this phenomenon we refer to the detailed considerations of PHILIPPI<sup>5)</sup>. His work makes it very probable that the decrease of  $\Delta V$  at increasing pH is not to be ascribed

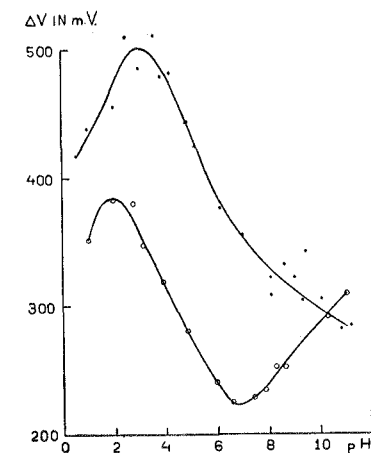


Fig. 5. Maximum surface potential differences of gliadin and gliadin-tannic acid films as a function of the pH.

● = curve for gliadin.  
○ = curve for gliadin-tannic acid.

to a change in the orientation of the molecules, but is caused by changes in the ionization of the protein and by changes in the electric double layer.

At low pH values the  $\Delta V$ -pH curves for gliadin-tannic acid films are of the same type as those for gliadin; only  $\Delta V$  is on a lower level. At pH = 7, however,  $\Delta V$  increases rather rapidly. This is caused by the gradual transition from the gliadin-tannic acid complex into gliadin at pH values above 7. At pH = 10–11 the influence of tannic acid has disappeared. This is in full agreement with the phenomena seen at film-pressure and compressibility measurements. The nearly constant  $\Delta V$  difference (about 140 mV.) between the complex and the gliadin films at pH values 1–7 indicates that in this region, presumably, a strongly ionized gliadin-tannic acid complex is present that is not influenced by the pH.

#### Viscosities of gliadin and gliadin-tannic acid films.

The viscosity of gliadin films is measured by determining the logarithmic decrement of torsion oscillations. The reproducibility was bad. When putting the torsion cylinder on the liquid surface and spreading after that, mostly a much lower viscosity was found than in case the cylinder was placed on the film already present; this must be caused by insufficient adherence of the film to the cylinder in the former case. We have, therefore, always applied the latter method. The lowering of the cylinder upon the surface had to be performed very carefully as small oscillations of the cylinder mostly gave very low viscosities (approximately those of pure water); this must be caused by disrapture of the film at the place of adherence as a result of the vibration. The viscosity proved to be highly dependent on the amplitude of the oscillations; the smaller the amplitude the greater the viscosity was. This proves that the viscosity is strongly influenced by the

shearing stress. The viscosities plotted in the graphs are those measured with the smallest amplitude (oscillation over about one degree). A more accurate establishment of the viscosity was of no avail with these inaccurate measurements. Above pressures of about 10 dn/cm the gliadin films showed elasticity; the period of oscillation decreased, at pressures of 20 dn/cm even to 6 sec. instead of 10.4 sec.

On measuring the viscosity of one film consecutively at different pressures a rather smooth viscosity-pressure curve was obtained; sometimes big differences from 100% more to 50% less were noticed, however, when duplicating the measurement on another film. We were strongly under the impression that these differences were due to small variations in the history of the film (e.g. time between spreading and measuring, velocity of blowing out the pipette); only, the exact reason we do not know. JOLY<sup>3)</sup> also noticed a strong influence of the history in the case of gliadin films; this author even distinguishes two types of films viz. highly viscous gel-like films, obtained by spreading in such a way that the pressure was high from the very beginning, and low viscous, non gel-like films obtained by spreading at a low initial pressure. These latter films remained, also at rather high pressures, relatively low viscous; the former films were more viscous according as the initial pressure was higher. In our method of spreading we could not obtain the low viscous type of films. The viscosities found in our measurements tally fairly well with those of the highly viscous films of JOLY.

The change in viscosity with pressure is shown in fig. 6 (curve I). All measurements were made by determining the damping of the oscillations. At a pressure of 6 dn/cm the

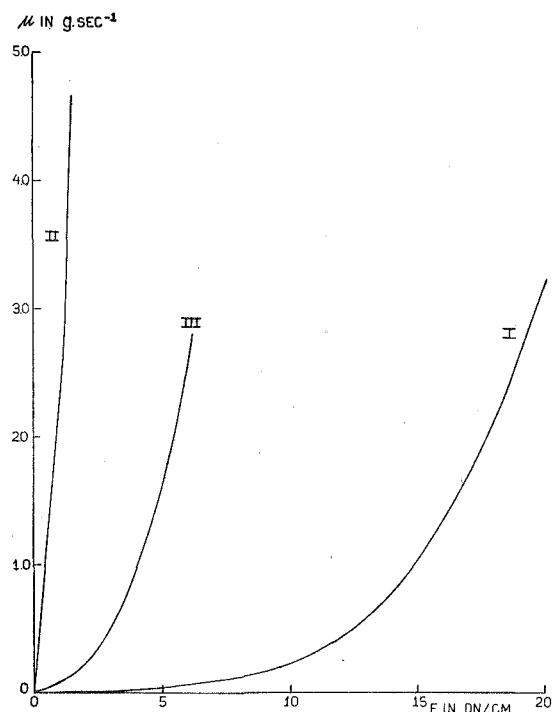
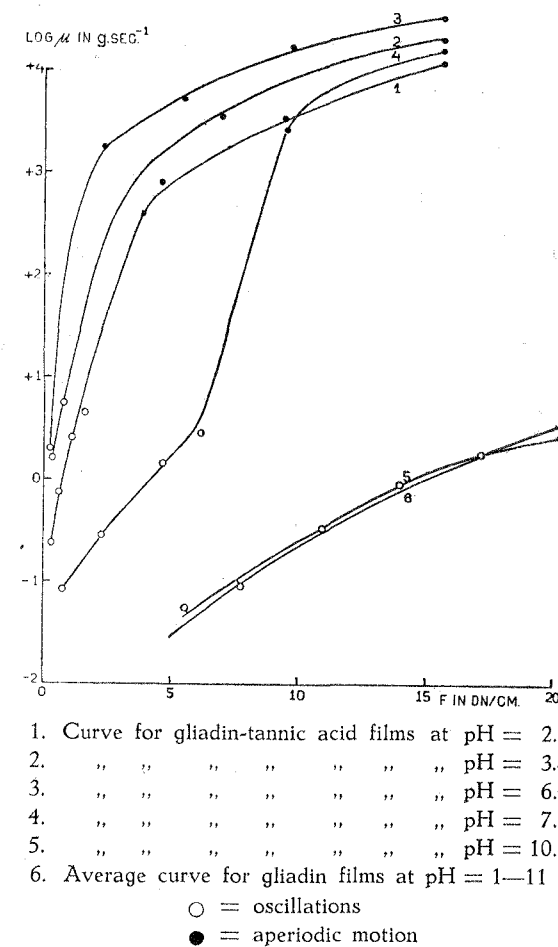


Fig. 6. Viscosity of gliadin films and of gliadin-tannic acid films at different surface pressures  $F$ .

- I average curve for gliadin films at pH = 1—11 and for a gliadin-tannic acid film at pH = 10.7  
 II „ „ for gliadin-tannic acid film at pH = 1—6.5  
 III „ „ for gliadin-tannic acid film at pH = 7.5

viscosity of gliadin films is, on an average, twice that of a surface of pure water (about 0.03 g sec.<sup>-1</sup>) and at a pressure of 8 dn/cm as much as 4 times as high. The curve drawn in fig. 6 (curve I) is the mean of 12 curves found for different pH values; we have refrained from drawing them separately as with these rather inaccurate measurements an influence of the pH could not be detected. The latter observation corresponds with the compressibility data where no influence of pH was found either.

Tannic acid proved to exert an enormous influence on the viscosity. Above pressures of 1—1½ dn/cm the measurement could not be made with oscillations anymore owing to the great damping; at pressures of 2—3 dn/cm, however, the motion was aperiodic and slow enough to render it possible easily to measure the decrease of amplitude with time. The rigidity of the films also appears when enlarging the area of spread; then the film tears which is easy to observe when strewing talc powder on it. The films are very elastic. After torsion the angular velocity of the cylinder was high in the beginning but then decreased, sometimes very slowly, till the shearing velocity became almost constant. Also at high film pressures where, owing to the high viscosity of the film, the decrease in amplitude was small (e.g. 10%), this phenomenon occurred, which proves that it is not due to a change of shearing velocity with shearing stress but is caused by elastic recovery.



1. Curve for gliadin-tannic acid films at pH = 2.0
2. „ „ „ „ „ „ „ „ pH = 3.8
3. „ „ „ „ „ „ „ „ pH = 6.4
4. „ „ „ „ „ „ „ „ pH = 7.5
5. „ „ „ „ „ „ „ „ pH = 10.7
6. Average curve for gliadin films at pH = 1—11

○ = oscillations  
 ● = aperiodic motion

Fig. 7. Viscosity (logarithmic scale) of gliadin-tannic acid films at different surface pressures  $F$ .

In order to collect all viscosities in one graph, those of gliadin films as well as those of gliadin-tannic acid films, we have plotted the viscosities on a logarithmic scale against the pressure in fig. 7. The values (mean from two series of observations) obtained from measurements with oscillations (viscosities lower than about 8 g sec<sup>-1</sup>) and those obtained from measurements with aperiodic motion (viscosities higher than about 200 g sec<sup>-1</sup>) prove to lie on a pretty smooth curve. From the curves it is again evident that above pH=7 the gliadin-tannic acid complex gradually passes into gliadin; at pH=11 the influence of tannic acid has disappeared.

Finally it may be mentioned that trials to spread a preparation of the compound gliadin-tannic acid failed as the compound could not be dissolved in an indifferent solvent. The compound was prepared by mixing solutions of gliadin in aqueous ethylalcohol with an excess of tannic acid in the same solvent; the precipitated complex was rinsed with the solvent and dried in vacuo.

*Summary.*

The properties of gliadin and gliadin-tannic acid films were studied by measuring the surface pressure, the surface potential and the surface viscosity. In particular the influence of the pH of the underlying solutions were examined. It was very striking that all these measurements tally very well and lead to the same results, which may be summarized as follows:

Gliadin films are of the liquid type; above pressures of about 7 dn/cm gelation occurs. At higher pressures the film becomes plastic and elastic without getting solid, however. At pressures higher than about 20 dn/cm the film shows signs of collapse. At the lower pressures presumably free water molecules are squeezed out of the spaces in and between the micellae. At higher pressures either the orientation of the polypeptid chains changes or hydration water bound to the polar groups of the gliadin is pressed out of the film.

Maximum spreading of gliadin occurs in the vicinity of the isoelectric point (pH about 6.5); the maximum is much flatter than that for most other proteins. At a pH below about 4.5 and higher than about 8.5 the area of spread on very diluted buffers becomes small, but remains greater than in the case of most other proteins. The solvent alcohol may be the cause of these phenomena.

With respect to the influence of electrolytes on the spreading, gliadin behaves like other proteins. The pH has little influence on the character of gliadin films, but chiefly influences the amount of gliadin that collects in the surface.

Tannic acid strongly affects the character of gliadin films. Below pH=7 tannic acid alters the film into a solid, very elastic one. At higher pH values the influence of tannic acid gradually decreases and at pH=11 it has quite disappeared. On compressing tannic-acid gliadin films at pressures above 0.5 dn/cm phenomena occur resembling collapse; according to our measurements these phenomena must be ascribed to squeezing out of hydration water and real collapsing only occurs at pressures above 30-40 dn/cm.

University Hospital, Clinic of Pediatrics, Leiden.

**Applied Mechanics.** — *On the state of stress in perforated strips and plates.* (2nd communication.) By K. J. SCHULZ. (Communicated by Prof. C. B. BIEZENO.)

(Communicated at the meeting of March 28, 1942.)

4. *Cartesian representation of the stresses corresponding to the functions U (3, 14).* The stresses, corresponding to the stress functions (3, 14), can easily be expressed in polar coordinates by using (2, 4). However, the series obtained in this way have a restricted domain of convergence, which makes them unsuitable for the calculation of the stresses in the points of a line  $z = c$  if  $c$  exceeds the limiting value  $b$ . Moreover, later on (see sect. 7) we shall need, particularly for points of such a line, cartesian expressions for the occurring stresses. Therefore we must construct other series, representing these stresses as Fourier series of the argument  $y$  and of the period  $b$ . To this end we refer to the function  $U_0$  (3, 8), which in consequence of (3, 10) can be written as follows:

$$U_0 = \Re \left\{ \ln x + \sum_{k=1}^{\infty} \left[ \ln \left( 1 - \frac{x}{kb} \right) + \ln \left( 1 + \frac{x}{kb} \right) \right] \right\} =$$

$$= \Re \left[ \ln \frac{x}{b} \left( 1 - \frac{x^2}{b^2} \right) \left( 1 - \frac{x^2}{4b^2} \right) \left( 1 - \frac{x^2}{9b^2} \right) \dots + \ln b \right]$$

if unessential constants are neglected. The expression between [ ] can be replaced by  $\ln \sin \pi x/b - \ln \pi/b$ , so that, with

$$\chi(x) = \ln \sin \pi x/b \dots \dots \dots (1)$$

$U_0$  may be represented by

$$U_0 = \Re \chi(x) \dots \dots \dots (2)$$

In order to deal with dimensionless numbers we introduce

$$\eta = 2\pi y/b, \zeta = 2\pi z/b, \xi = \eta + i\zeta = 2\pi(y + iz)/b = 2\pi x/b \dots (3)$$

The function  $\chi(x) = \ln \sin \xi/2$  can then be expanded into the following series

$$\chi(x) = \ln \left[ -\frac{i}{2} \left( e^{\frac{i\xi}{2}} - e^{-\frac{i\xi}{2}} \right) \right] = \ln \left[ \frac{ie^{-\frac{i\xi}{2}}}{2} (1 - e^{i\xi}) \right] =$$

$$= -\frac{1}{2} i\xi - \ln 2 + \frac{i\pi}{2} + \ln(1 - e^{i\xi}) =$$

$$= \ln \left[ -\frac{ie^{\frac{i\xi}{2}}}{2} (1 - e^{-i\xi}) \right] = +\frac{1}{2} i\xi - \ln 2 - \frac{i\pi}{2} + \ln(1 - e^{-i\xi}).$$