# The Relaxation Time and Dipole Moment of Gliadin

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ours and Getman's on the whole somewhat above. Quintin's measurements, on the other hand, show a definite drift when compared with our data, her e.m.f. being smaller at lower concentrations and greater at high concentrations. The entry for 25°C in Table V is in agreement with the mean of the previous results for the saturated cell.

As we have mentioned above, Lebettre[3] on the basis of his results for the cell Cu amalgam/$CuSO_4/PbSO_4$, Pb, has computed activity coefficients from measurements extending down to solutions as dilute as 0.001 molal; his coefficients are in complete disagreement with those listed in Tables II and III and with the freezing point data, and, moreover, correspond to a La Mer "$a$" parameter[10] of only 2.4A—an extraordinarily small value. It seems to us that the most probable explanation of his results is that the copper sulphate in his most dilute solutions was partially hydrolyzed and that as a result his effective cupric ion concentrations were less than he supposed. The entry in Table III for 0.01 $m$, computed from freezing point and heat of dilution data, corresponds to an "$a$" of 3.9A—a more reasonable value in view of the results that have been obtained for other bivalent sulphates.[11]

[10] Gronwall, La Mer and Sandved, Physik. Zeits. **29**, 358 (1928).

[11] See, for example, La Mer and Parks, J. Am. Chem. Soc. **53**, 2040 (1931), Cowperthwaite and La Mer, J. Am. Chem. Soc. **53**, 4333 (1931), and reference 10.

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# The Relaxation Time and Dipole Moment of Gliadin

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THE dielectric constant of a medium depends not only on the temperature and concentration but also on the frequency. This is due to the fact that the molecules cannot orient themselves instantaneously with their electrical charges against the field when the latter changes rapidly. Accordingly Debye[1] writes the Clausius-Mosotti formula in the following manner:

$$\frac{\epsilon-1}{\epsilon+2}\frac{M}{d}=\frac{4\pi N}{3}\left(\alpha_0+\frac{1}{3kT}\cdot\frac{\mu^2}{1+i\omega\tau}\right). \quad (1)$$

In this equation $\epsilon=\epsilon'-i\epsilon''$ ($\epsilon'$ being the real part of the dielectric constant or that which is measured and $\epsilon''$ the imaginary part which cannot be measured by capacity methods), $M$ is the molecular weight, $d$ is the density of the medium, $N$ is the Avogadro number, $\alpha_0$ is the optical polarisation, $\mu$ is the dipole moment, $\omega=2\pi\nu$ is the frequency, $\tau$ is the relaxation time, $T$ is the absolute temperature and $k$ is the Boltzmann constant.

If the frequency is of the order of that of light formula (1) reduces to

$$\frac{\epsilon_0-1}{\epsilon_0+2}=\frac{4\pi N\alpha_0}{3}, \quad (2)$$

and if the frequency is (small or) zero (direct current field) the formula reduces to the following

$$\frac{\epsilon_\infty-1}{\epsilon_\infty+2}=\frac{4\pi N}{3}\left(\alpha_0+\frac{\mu^2}{3kT}\right). \quad (3)$$

By combining formulas 1, 2, and 3 and solving for the real part of $\epsilon$ we obtain

$$\epsilon'=\epsilon_0+(\epsilon_\infty-\epsilon_0)\Big/\left(1+\left(\frac{\epsilon_\infty+2}{\epsilon_0+2}\right)^2\omega^2\tau^2\right). \quad (4)$$

By remembering that it is necessary to exert a torque to rotate a spherical molecule against the inner friction of the medium in which it is suspended the time of relaxation of such a molecule may be expressed in terms of its radius to give the following important result[8]

$$\tau=\frac{4\pi\eta r^3}{kT}=\frac{\epsilon_0+2}{\epsilon_\infty+2}\cdot\frac{1}{2\pi\nu_c}. \quad (5)$$

The frequency $\nu_c$ is that frequency for which $\epsilon=(\epsilon_\infty+\epsilon_0)/2$.

But if the molecule is a rotation ellipsoid with its long axis equal to $a$, and the short axis to $b$,

$(b/a=\rho)$ and it is rotating around its long axis in a medium with the viscosity $\eta$, then F. Perrin[7] has shown that the relaxation time is

$$\tau=\frac{4\pi ab^2\eta}{kT}\cdot\psi=\frac{4\pi ab^2\eta}{kT}\frac{4}{3}$$

$$\times\frac{1-\rho^4}{1+(2\rho^2-1)(\rho^2/\sqrt{(1-\rho^2)})\ln(\sqrt{(1-\rho^2)}/\rho)}. \quad (6)$$

Now $4\pi ab^2/3=MV/N$ where $M$ is the molecular weight and $V$ the specific volume of the solute.

The molecular weight is obtained from centrifuge data according to the following formula:

$$M=RTs/D(1-Vd), \quad (7)$$

where $s$ is the sedimentation constant, $D$ is the diffusion constant, and $d$ is the density, all in water at the temperature 20°C.

Finally, by combining Eqs. (6) and (7), we obtain

$$\tau=\frac{3\eta s}{D(1/V-d)}. \quad (8)$$

## Preparation of gliadin

The object of this research was to study the relaxation time of gliadin with regard to the foregoing theory. The molecular weight and stability of this protein have been studied in this laboratory by Svedberg and Krejci[4] and its diffusion and viscosity in solution have been studied by Lamm and Polson,[5] also in this laboratory.

Neither the method of preparing gliadin of T. B. Osborne[6] nor that of Haugaard and Johnson[2] were suitable for our purpose; the former uses ether and absolute alcohol, which may probably denature the gliadin, whereas the latter separates the different components by flotation in LiCl and NaCl solutions. The high conductivity of solutions containing protein which had been in contact with appreciable electrolyte would render them unsuitable for capacity work.

The gliadin was prepared in the following manner: 1500 g flour was slowly added with constant stirring to 3000 cc aqueous alcohol (64 percent by weight). After having stirred for one-half day the solution was filtered through cotton cloth and put into a refrigerator at −8°C for four days. It was filtered at this temperature. It was then evaporated by using suction. When most of the alcohol had been removed the main part of the gliadin settled to the bottom of the vessel and the supernatant solution containing water soluble substances and some gliadin was discarded. The residue was fully dried and afterwards dissolved in alcohol. Three solutions were studied, one ($A$) containing 2.91 percent (weight) gliadin in 61.2 percent alcohol, a second ($B$) containing 1.70 percent in 46.9 percent alcohol, and a third ($C$) with 3.94 percent gliadin in 62.8 percent alcohol. (Maximum solubility = 4.01 percent in 61.7 percent alcohol.) Each sample was dialysed against alcohol of the same concentration. The outer liquids from dialyses were used as standards in all measurements.

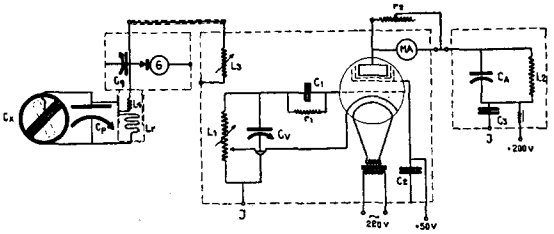

FIG. 1. Resonance apparatus for dielectric constant measurements.

$C_x$ = Capacity cell (the positions marked)
$C_p$ = Precision condenser 1500 $\mu\mu F$ or 500 $\mu\mu F$
$C_v$ = Variable condenser, 100 cm
$C_A$ = Variable condenser 450 cm
$C_1$ = Fixed condenser 250 cm
$C_2$ and $C_3$ = Fixed condenser 5000 cm
$L_1$, $L_2$, $L_3$, $L_4$, and $L_r$ = Variable inductances
$r_1$ = Fixed resistance, 5000Ω
$r_2$ = Variable resistance 0–310Ω (Shunt for $A$)
$MA$ = Milliammeter
$G$ = Galvanometer (Weston)
Tube = Philips E 446 transmitting tube
$J$ = Earth connections of shield.

## Ultracentrifuge measurements

The samples were run in the ultracentrifuge (70,000 r.p.m.) corresponding to 350,000 times gravity, and the sedimentation constants (reduced to water) were found to be, for solution $A$, $s=1.94\times10^{-13}$, for $B$, $s=2.01\times10^{-13}$, and for $C$, $s=2.04\times10^{-13}$. The corresponding molecular weights are $A=27{,}500$, $B=28{,}500$, and $C=28{,}900$. The ultracentrifuge diagrams showed no evidence of heavier particles or inhomogeneities. However, to make certain of a reproducible and homogeneous product, it is advisable to filter the sample at −11° and wash the precipitate with 5 percent alcohol.

## Dielectric constant measurements

The dielectric constants of the several gliadin solutions under investigation have been measured

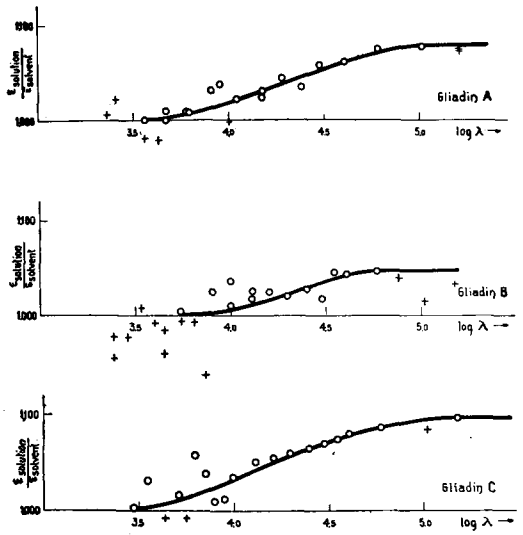


FIG. 2. Ratio of dielectric constant of solution to that of solvent as function of logarithm of wave-length. Actual dielectric constants may be obtained by multiplying the ratio by 43.8 for gliadin *A*, 57.5 for gliadin *B* and 42.7 for gliadin *C*.

with radiofrequency bridge or with resonance circuits, depending upon the frequency used. In the construction of the apparatus and in the capacity measurements directions given in a recent laboratory manual[9] were followed. The dielectric cells used were especially constructed to give proper shielding, rapid heat exchange with thermostat bath, low capacitative and inductive effects between leads, and exactness in operation. In these cells the capacity is measured with the rotor in two different positions without changing the external connections to the cell.

TABLE I. *Dielectric constant and time of relaxation data for gliadin solution A.*

| $\lambda_m$ | $\epsilon_{SOLUTION}/\epsilon_{SOLVENT}$ | $\tau_{SEC.} \times 10^8$ |
|---|---|---|
| 1600 | 1.073 | |
| 1600 | 1.071 | |
| 1030 | 1.077 | |
| 591 | 1.074 | 7.0 |
| 403 | 1.067 | 10.5 |
| 300 | 1.057 | 9.0 |
| 240 | 1.035 | 13.1 |
| 191 | 1.044 | 8.3 |
| 149 | 1.030 | 9.3 |
| 149 | 1.024 | 11.0 |
| 110 | 1.022 | 8.7 |
| 89.5 | 1.038 | 4.5 |
| 80.5 | 1.031 | 4.9 |
| 62.2 | 1.008 | 9.1 |
| 54.7 | 1.009 | 7.5 |
| 47.0 | 1.010 | |
| 36.3 | 1.000 | |

Between $\lambda = 100$–$1600$ m the bridge method was used. A Hartley oscillator with modulated carrier wave (1000 cycles from amplified microphone hummer) was used as a generator. An ordinary radio receiver served as a detector for the wave-lengths 250–1600 m, but a specially built receiver was necessary for wave-lengths less than 250 m. Two mica condensers of 2000 cm capacity were used as the first two sides of the bridge; in the third a 2000 cm mica condenser parallel to a 0–1000Ω pressure resistance was used. The fourth side of the bridge contained the cell, the precision condenser, a simple variable condenser and an electrolyte resistance. The largest error in the measurement with this bridge is due to variations in the electric field of the laboratory.

The connections for the resonance circuit are

TABLE II. *Dielectric constant and time of relaxation data for gliadin solution B.*

| $\lambda_m$ | $\epsilon_{SOLUTION}/\epsilon_{SOLVENT}$ | $\tau_{SEC.} \times 10^8$ |
|---|---|---|
| 1500 | 1.033 | |
| 1030 | 1.015 | |
| 761 | 1.039 | |
| 591 | 1.046 | 6.3 |
| 403 | 1.044 | 6.2 |
| 350 | 1.045 | 4.6 |
| 300 | 1.017 | 20.6 |
| 250 | 1.027 | 11.2 |
| 198 | 1.020 | 11.9 |
| 160 | 1.024 | 8.1 |
| 130 | 1.025 | 6.2 |
| 129 | 1.017 | 8.8 |
| 100 | 1.010 | 9.9 |
| 100 | 1.035 | 3.1 |
| 80.5 | 1.025 | 3.9 |

TABLE III. *Dielectric constant and time of relaxation data for gliadin solution C.*

| $\lambda_m$ | $\epsilon_{SOLUTION}/\epsilon_{SOLVENT}$ | $\tau_{SEC.} \times 10^8$ |
|---|---|---|
| 1500 | 1.097 | 7.4 |
| 1030 | 1.085 | 19.5 |
| 591 | 1.087 | 10.2 |
| 403 | 1.080 | 9.3 |
| 350 | 1.075 | 9.4 |
| 300 | 1.070 | 9.2 |
| 250 | 1.065 | 8.6 |
| 197.5 | 1.060 | 7.6 |
| 160.5 | 1.055 | 6.9 |
| 130 | 1.051 | 6.1 |
| 100 | 1.035 | 6.5 |
| 89.5 | 1.012 | 11.6 |
| 79.1 | 1.010 | 11.4 |
| 71.8 | 1.038 | 4.4 |
| 62.2 | 1.058 | 2.5 |
| 36.2 | 1.031 | 2.6 |
| 30.0 | 1.003 | 8.2 |
| 57.6 | 1.016 | 5.7 |

shown in Fig. 1. The galvanometer is in the step over circuit, which is also tuned. The coupling coils to the resonance circuit are movable in a shielded box, so that any outside field will not cause disturbances.

## Conclusions

The values of the dielectric constants of the solutions were never more than 1.1 times that of the solvent. Thus, an error in the third decimal place in capacity values will cause a large error in the relaxation time. All values are given for 20°C. The curves in Fig. 2 (gliadin solutions $A$, $B$, and $C$) show the variation of the ratio between the dielectric constant of the solution and that of the solvent with the logarithm of the wave-length.

In making the calculations for the times of relaxation of the gliadin molecules use has been made of refractive index data to evaluate the constant $\epsilon_0$. We have taken arbitrarily $n^2=\epsilon_0$. The refractive indices for gliadin solutions are taken from an equation of Kent Jones and Amos[3] as follows:

$$n_{\text{gliadin}}=n_{\text{alcohol}}+0.0018C \quad (C=\text{concentration in weight percent}).$$

This equation gives practically the same value of $n^2=\epsilon_0$ for the solutions as for the solvent. The curves have been drawn by using all experimental points but only those for which $\epsilon_{\text{solution}}/\epsilon_{\text{solvent}}>1.000$ have been used in the calculation. Our choice of $\epsilon_0$ is such that if this ratio is equal to or less than unity imaginary values of $\tau$ will result.

In order to calculate the $\tau$ values for gliadin solution $A$, $\epsilon_\infty$ has been fixed as $1.078\times 43.8=47.2$; for gliadin $B$, $\epsilon_\infty=1.048\times 54.9=57.5$; and for gliadin $C$, $\epsilon_\infty=1.098\times 42.7=46.9$. The solvent dielectric constant values are 43.8, 54.9 and 42.7, respectively. The average values of $\tau$ are calculated to be $8.9\times 10^{-8}$ sec. for gliadin $A$, $8.9\times 10^{-8}$ sec. for gliadin $B$ and $8.5\times 10^{-8}$ sec. for gliadin $C$. The values represent molecular weights of 28,000 for gliadin $A$, 25,500 for gliadin $B$ and 27,000 for gliadin $C$. The dielectric constant data (Tables 1, 2 and 3) do not indicate any polydispersity of the gliadin.

On the other hand, if the values of $s$, $D(6.78\times 10^{-7}$, Lamm and Polson[5]), $b/a(0.1041$, Lamm and Polson[5]), and $V(0.745$, Krejci and Svedberg[4]) are substituted in the formula (8) we obtain for the relaxation time for gliadin $A$, $\tau=8.99\times 10^{-8}$ sec., for gliadin $B$, $\tau=10.26\times 10^{-8}$ sec. and for gliadin $C$, $\tau=9.37\times 10^{-8}$ sec. The relaxation time for a gliadin suspended in pure water is calculated to be $\tau=3.7\times 10^{-8}$ sec. at 20°C.

The times of relaxation given above are for the electrical field rotations of the gliadin molecule about the long axis. In order to obtain the constants characteristic of the rotation about the short axis dielectric constant measurements at longer wave-lengths are necessary. According to a private communication such data have been obtained recently for zein dissolved in aqueous alcohol solvent by Williams and Elliott working in the Wisconsin laboratory.

The dipole moment of the solute was calculated to be $14.3\times 10^{-18}$ e.s.u., $12.6\times 10^{-18}$ e.s.u., and $13.7\times 10^{-18}$ e.s.u. for gliadin $A$, $B$, and $C$, respectively. As an average value we give $\mu=13.5\times 10^{-18}$ e.s.u.

I wish to express my sincere thanks to Professor J. W. Williams of the University of Wisconsin for his friendly help and his interest in opening this inspiring chapter of the physical chemistry to me, and to Professor The Svedberg, who has helped me in performing my work. I also wish to thank Mr. A. Polson of this institute for putting diffusion data at my disposal.

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