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Dielectric Constant Studies. III. Aqueous Gelatin Solutions

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Measurements have been made of the dielectric constant of gelatin solutions. A test of the Bjerrum "Zwitter-ionen" theory was furnished by a study of the effect of pH on the dielectric constant as measured by the Drude method; the data obtained support the theory. Through the application of an equation suggested by Marinesco, an attempt was made to determine the amount of water fixed by gelatin; if this equation is valid for gelatin the results obtained for absorbed water must be interpreted as indicating that the water bound by the gelatin is still free to show its dielectric properties. By means of another equation given by Marinesco relating dielectric absorption with molecular weight, values were calculated for the molecular weight of gelatin; the results obtained are consistent with those given by other methods.

BECAUSE of the probable dipole nature of proteins, it should be possible to obtain some valuable information concerning their properties through dielectric constant measurements. Thus, a test of Bjerrum's "Zwitter-ionen" theory of ampholytes might be possible. If this theory of ampholytes is correct, one would expect that gelatin, at its isoelectric point, should show a maximum dielectric constant; and the addition of either acid or base to isoelectric gelatin should cause a decrease. Again, the ultimate nature of a gel is a problem of considerable importance. What forces bind the water and maintain a solid condition even though the proportion of water is greater than 95 percent? No satisfactory answer has yet been made to this question. That the forces are electrostatic is often stated. A study of the dielectric constant of gelatin solutions under a variety of conditions offers a possible approach to this problem. If the water is bound, the dipoles are no longer free to orient and this part of the dielectric constant is decreased.

Another possible application of dielectric constant measurements to proteins is the determination of their apparent molecular weights.

A review of the investigations on gelatin shows a contradiction in the results. Thus Drude[1] and Fürth[2] found a decrease in the dielectric constant of gelatin solutions with increase in concentration. These investigators, however, did not consider the effect of pH. Marie and Marinesco,[3] on the other hand, working apparently with more care in respect to pH of the gelatin and the manner of its preparation, found a rise of the dielectric constant with increase in concentration. The contradiction in these results has not been satisfactorily explained. It may be due to the difference in the frequency employed. Drude and Fürth used a 76-centimeter wave while Marie and Marinesco used a six-meter wave. The possibility also exists that one or both sets of results do not represent true dielectric constants because of the uncertain influence of the conductivity of the solutions or other factors.

While the present work was in progress, Marinesco[4] published a comprehensive paper on the proteins. Work has been done, also, by Fricke[5] and by May and Schaffer.[6]

APPARATUS AND MATERIALS

The methods used in this work are described in Papers I and II of this series.* A Drude method was used with the shorter waves and the resonance method with the longer waves. The range of wave-lengths available was from 3.5 to about 100 meters.

[1] Drude, Zeits. f. physik. Chemie **23**, 267 (1897).
[2] Fürth, Ann. d. Physik **70**, 63 (1923).
[3] Marie and Marinesco, J. chim. phys. **27**, 455–70 (1930).
[4] Marinesco, J. chim. phys. **28**, 51 (1931).
[5] Fricke, Kolloid Zeits. **56**, 166 (1931).
[6] May and Schaffer, Zeits. f. Physik **73**, 452 (1931).
* J. Chem. Phys. **1**, 836, 842 (1933).

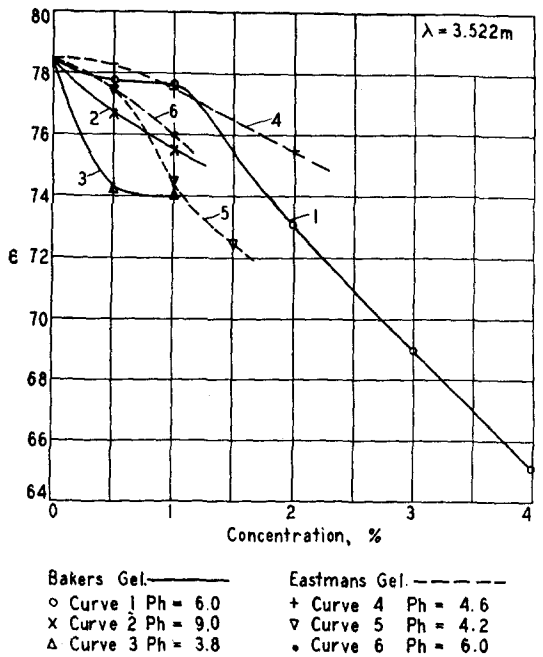


FIG. 1. Effect of concentration on the dielectric constant of gelatin solutions as measured by the Drude method at various values of pH.

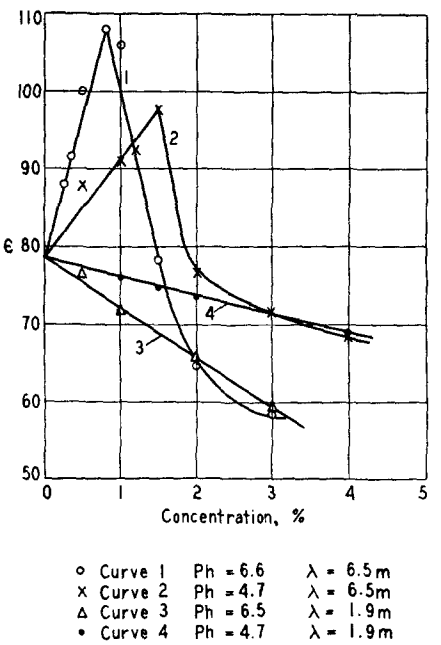


FIG. 2. Effect of concentration on the dielectric constant of gelatin solutions at different values of pH. Results of Marinesco.

The materials used were Baker's commercial gelatin and Eastman's isoelectric gelatin. Two samples of the latter were obtained, representing two different lots. The Baker gelatin contained about 1.5 percent ash, chiefly calcium salts. The Eastman product was practically ash-free. A glass electrode apparatus was used for measuring the pH. All solutions were prepared at 50°C. The pH was adjusted by adding NaOH or HCl in dilute solution to the solution of gelatin.

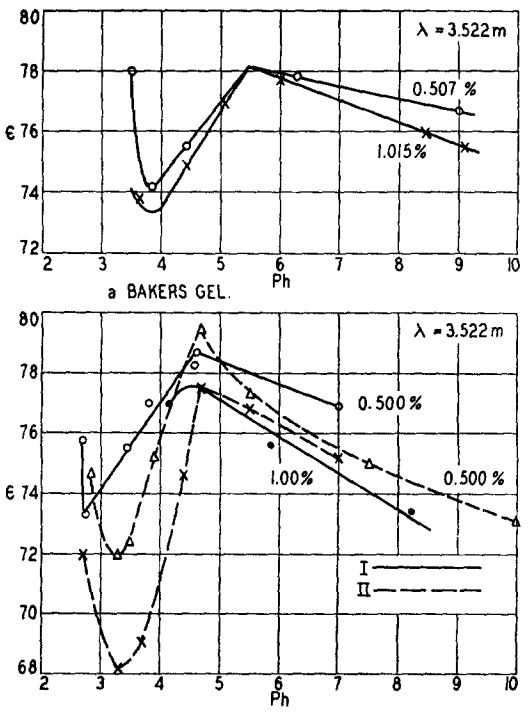
DISCUSSION OF RESULTS

A series of measurements was made at constant frequency (3.522m) with different concentrations of gelatin. The results obtained are shown by Fig. 1. The dielectric constants** are plotted as ordinates and the concentrations as abscissae. For comparison the results of Marinesco are given in Fig. 2. From these curves in Fig. 1 it may be observed that in general there is a decrease of the dielectric constant with increase in concentration of gelatin. Isoelectric gelatin, however, in the lower concentrations, gives a slight rise, as shown by curve 4.

It may be observed, also, as is shown better in Figs. 3a and b, that the dielectric constant of gelatin appears to decrease on either side of the isoelectric point; similar results were obtained by Marinesco at low wave-lengths, as may be deduced from curves 3 and 4 of our Fig. 2 of his data. These results are in agreement with Bjerrum's theory as outlined above.

At the longer wave-lengths, it is found by comparison of the values obtained by the authors (Fig. 4) with those of Marinesco (Fig. 2, curves 1 and 2) that there is no agreement. Marinesco finds a sharp rise of the dielectric constant with concentration of gelatin to a maximum which appears at a concentration of 1.5 percent in case of isoelectric gelatin, and at 0.75 percent for a gelatin of pH 6.6. After the maximum is reached, the fall with concentration is rapid until the dielectric constants measured agree with those at the lower wave-lengths.

** In place of the term, dielectric constant, the term, "square of the index of refraction," should be substituted in this case, for the values given are uncorrected for any effects of conductivity; and, in general, the n^2 term is larger than ϵ. The term, dielectric constant, will be used for convenience, however, in the whole discussion.



FIGS. 3a and b. Effect of pH on the dielectric constant of gelatin solutions as measured by the Drude method at various concentrations.

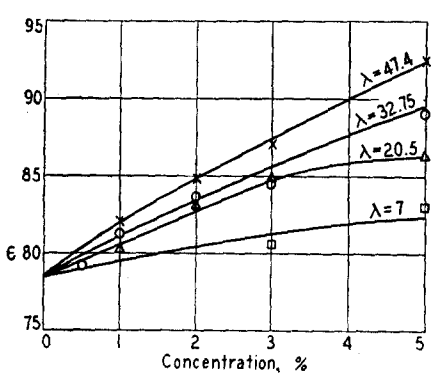


FIG. 4. Effect of concentration and of wave-length on the dielectric constant of isoelectric gelatin solutions as determined by the resonance method.

On the other hand, the values obtained by the present authors show no such sudden rises and attain no maximum within the concentration range studied, although the rate of increase of dielectric constant with concentration at the longer wave-lengths does fall off somewhat in the higher concentrations. Marinesco attributes the rise of dielectric constant to the effect of the dipoles of the gelatin molecules and the abrupt decrease to the union of dipoles to form nonpolar groups. Our results give no evidence of such a coupling; the slight flattening of the curves at the higher concentrations may properly be associated with the increased viscosity.

As previously mentioned, dielectric constant studies should give some information concerning the association of gelatin molecules with molecules of the solvent. In an aqueous gelatin solution there are presumably four factors which may contribute to the total dielectric constant. They are (1) water molecules with the dipoles free, for which $\epsilon=78.57$ at 25°C; (2) water molecules the dipoles of which are fixed, $\epsilon=2.2$; (3) gelatin molecules with dipoles not orienting in the field, $\epsilon=5.4$; (4) gelatin molecules, the dipoles of which are free. The gelatin aggregates are large and it should be possible to make the frequency so high that they cannot orient. If such were the case, the fourth factor above would disappear and the dielectric constant of the solution would be determined only by the other three.

Following Marinesco, it may be shown that if N_1, N_2 and N_3 represent the number of grams of free water, of fixed water and of dissolved gelatin in 1 cc of solution; and d_1, d_2 and d_3 represent the corresponding densities, the following relationship exists:

$$\frac{\epsilon-1}{\epsilon+2}\left(\frac{N_1}{d_1}+\frac{N_2}{d_2}+\frac{N_3}{d_3}\right)=N_1p_1+N_2p_2+N_3p_3. \quad (1)$$

Let $S=N_1+N_2=$ total g of water in 1 cc and consider $d_1=d_2$, then

$$\frac{\epsilon-1}{\epsilon+2}\left(\frac{S}{d_1}+\frac{N_3}{d_3}\right)=(S-N_2)p_1+N_2p_2+N_3p_3. \quad (2)$$

p_1, p_2 and p_3 represent the specific polarizations of free water, of electrically saturated or fixed water and of solid gelatin, respectively. Since $S/d_1+N_3/d_3=1$ (the unit of volume of the solution), then by substituting in (2) and transforming,

$$N_2=(Sp_1+N_3p_3-[(\epsilon-1)/(\epsilon+2)])/(p_1-p_2). \quad (3)$$

It should be possible by Eq. (3) to calculate the number of grams of water per cc, the dipoles of which are fixed, provided the p values are known

for fixed and free water and for gelatin with fixed dipoles.

The necessary values were obtained and the amounts of fixed water were calculated from our own data at 3.522 meters, as well as from Marinesco's data at 1.9 meters. These values are recorded in Table I. The first column gives the

TABLE I. *Fixation of water molecules by gelatin.*

pH	Spec. vol. gelatin	p_3	N_3	S	ϵ of solution	$\frac{\epsilon-1}{\epsilon+2}$	H
6.6	.724	.4488	.005	.9964	76.4	.9617	.131
6.6	.724	.4488	.01	.993	71.8	.9593	.270
6.6	.724	.4488	.02	.9855	65.6	.9554	.110
			Baker's gelatin measurements by authors				
6.6	.790	.491	.01015	.9920	77.1	.9621	−.2665
6.6	.790	.491	.00507	.9961	77.9	.9621	−.1745
6.6	.790	.491	.0203	.9842	76.3	.9617	−.289
3.8	.790	.491	.00507	.9961	74.5	.9608	.296
3.8	.790	.491	.01015	.9920	73.0	.9600	.0443
			Eastman's gelatin measurements by authors				
6.6	.790	.491	.01015	.9920	75.2	.9602	−.1328
8.2	.790	.491	.01015	.9920	73.5	.9617	.0147
3.8	.790	.491	.00446	.9965	76.3	.9617	.0663
2.76	.790	.491	.00446	.9965	73.3	.9602	.553

$p_1 = 0.9630$
$p_1 - p_2 = 0.6765$

pH of the solutions; the second, the specific volume of solid gelatin; the third, p_3, or the specific polarization of solid gelatin; the fourth, the concentration of gelatin in grams per cc; the fifth, S, the total grams of water per cc; the sixth, ϵ, the dielectric constant of the solution. The last column, H, contains the calculated values for the grams of water fixed per gram of gelatin, which may be simply calculated from N_2 of Eq. (3). In the use of this formula p_3 was calculated by using Fürth's value of 5.9 for the dielectric constant of solid gelatin.

It is clear from our results, which give, in some cases, negative values for H, that this method cannot be used to determine the extent to which water is bound by gelatin. Although it is possible that the frequency used was not high enough completely to prevent the rotation of the gelatin molecules, a more likely interpretation of the results is that the water bound by the gelatin is still partially free to show its dielectric properties.

The determination of molecular weights by means of dielectric constant measurements is based upon the equation given by Marinesco in the form

$$M = \tfrac{1}{3}(\lambda/C)(RT/\eta V),$$

where

M = molecular weight
T = temperature; here 298°K
η = viscosity of solvent; here 0.011 poises
λ = wave-length in region of dispersion
R = gas constant; 83.2×10^6 ergs/degree
V = specific volume of the material in solution; here 1.38 cc/gm
c = velocity of light, 3×10^{10} cm/sec.

Since dispersion was found from 7 meters to 50 meters, the molecular weights indicated range from 13,500 to 96,300. Gelatin appears, therefore, to possess molecules of different molecular weights. Although this method is yet unproved, the values obtained are reasonable at least. The use of the ordinary viscosity as the effective viscosity acting on the molecules is of course open to question.

It is noteworthy that the dielectric constant of a gelatin solution is unaffected by the setting of the solution to give a solid. Solutions show a higher dielectric constant when first prepared and this gradually decreases, but the rate is not influenced by the setting, at least so far as may be observed. When a solution has visibly set, the dielectric constant continues to fall for some hours thereafter, although with a decreasing rate.

These observations, while in agreement with those of Fricke,[5] are not in agreement with those of Marinesco.[4] Marinesco assumes that the maximum of the dielectric constant-concen tration curve (Fig. 2, curve 1) determined at 6.5 meters wave-length has a unique significance He attributes the rapid rise in dielectric constant of the solution to the dipole nature of the molecules of added gelatin. At the concentration 0.75 percent, which is for the apex of the curve, he assumes the dipoles to combine and thus produce a rapid decrease in dielectric constant of the solution with increase in concentration. He further states in the case of solutions of pH 6.6 that the apex of the curve represents the concentration at which gel formation is first possible. This explanation is not satisfactory because the same reasoning cannot be applied to isoelectric gelatin, since the maximum in this case is at about 1.5 percent concentration, while

it is well known that isoelectric gelatin will set before that concentration is reached and also that gelatin sets most readily at the isoelectric point and not least readily, as Marinesco's interpretation would lead us to believe.

The picture of the nature of gelatin solutions that may be drawn from our data is approximately the conventional one. The gelatin molecules or particles in suspension are of graded size and of rather large molecular weights, ranging at least from about 5000 to 100,000. The gradation in size of molecule is apparently a continuous one, although gradations in steps of the order 10,000 are not excluded by the accuracy of the data obtained. This method does not exclude the possibility of other molecules or aggregates being present so long as they have no dipole moment. This situation is not likely in the case of proteins because of the large moments consistently obtained for the amino acids which are their decomposition products. It appears, also, that no coupling of the dipoles occurs and that gel formation is unaccompanied by any marked change in the dielectric properties.