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The Influence of Electrolytes on the Cataphoretic Charge of Colloidal Particles and the Stability of Their Suspensions

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THE INFLUENCE OF ELECTROLYTES ON THE CATAPHORETIC CHARGE OF COLLOIDAL PARTICLES AND THE STABILITY OF THEIR SUSPENSIONS.

II. Experiments with Particles of Gelatin, Casein, and Denatured Egg Albumin.

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(Received for publication, August 22, 1922.)

I.

Hardy observed that the stability of suspensions of particles of boiled white of egg was a minimum at the isoelectric point and he correlated this observation with another fact discovered by him that the particles are not charged at the isoelectric point, assuming that the stability of suspensions is determined by the electrostatic repulsion of the particles on account of the fact that they are surrounded by double electrical layers. He furthermore explained the precipitation of colloidal suspensions by salts or electrolytes in general by the assumption of an annihilation of the electrical charges of the particles.[1]

Since many proteins are least stable at the isoelectric point, the conclusion was drawn by some authors that even genuine proteins never form crystalloidal solutions, but that their particles are surrounded in water by electrical double layers and are prevented from coalescing through the electrostatic repulsion determined by these layers. The precipitation of genuine proteins from their aqueous solutions by salts was then also explained by the assumption that it was due to the annihilation of these double layers.

While Hardy's observations and conclusions were correct as far as the insoluble particles of boiled white of egg were concerned, it was difficult to harmonize them with observations on certain genuine

[1] Hardy, W. B., *J. Physiol.*, 1905–06, xxxiii, 251.

proteins. Aqueous solutions of crystalline egg albumin at the pH of the isoelectric point will remain stable for a year (if not permanently) if the temperature is not too high, and since the particles have no cataphoretic charge at this pH, it is obvious that they must be kept in solution by forces other than those due to cataphoretic charges, on which the stability of solutions of the same protein depends when it is denatured by heat. The only other forces which can keep proteins in solution are the forces which determine the solubility of crystalloids. This idea is supported in the case of solutions of genuine crystalline egg albumin by viscosity measurements. The writer has shown that whenever a protein solution contains suspended particles (capable of occluding water and of swelling) the viscosity is of a much higher order of magnitude than that of solutions of crystalloids, and that this high viscosity is influenced by acids and alkalies in a similar way as is the osmotic pressure. He found that the viscosity of solutions of crystalline egg albumin is of a comparatively low order of magnitude and is not influenced by acids or alkalies in the same way as is the osmotic pressure.[2] From these observations on the viscosity of the solutions of crystalline egg albumin as well as from the fact that the solutions of this protein of a concentration of 8 per cent or more are stable at the isoelectric point, the inference must be drawn that the forces which keep genuine crystalline egg albumin in solution are of the same nature as the forces which keep crystalloids in solution. These latter forces are, according to Langmuir and Harkins, forces of chemical attraction between solute (or certain chemical groups of the solute) and the solvent—in this case water. These forces may or may not be secondary valency forces. There is a criterion which permits us roughly to decide which of the two kinds of forces determines the stability of solutions, the forces active in crystalloidal solutions (secondary valency forces) or the forces active in colloidal suspensions (electrical double layers). The P.D. of electrical double layers is reduced to zero by comparatively low concentrations of salts and the active ion has always the opposite sign of charge to that of the particle. No such relation exists in the case of crystalloidal solutions, and salts might even increase the solubility of a crystalloid in water.

[2] Loeb, J., Proteins and the theory of colloidal behavior, New York and London, 1922, 195; *J. Gen Physiol.*, 1920–21, iii, 827.

When this criterion is applied to solutions of certain genuine proteins such as crystalline egg albumin or gelatin, it is found that high concentrations of salts, *e.g.* NaCl or $CaCl_2$, are required for precipitation and that the effective ion of the salt has no relation to the sign of charge of the protein particle. Thus sulfates are generally better precipitants for solutions of genuine egg albumin and gelatin than chlorides, regardless of whether the protein is negatively or positively charged, or not charged at all. To escape the conclusion that genuine proteins form true solutions in water, some colloid chemists suggested that genuine proteins should be called emulsoids, thereby insinuating that such proteins as genuine egg albumin or gelatin form diphasic systems of the type of emulsions of oil in water. It is true that the stability of droplets of pure oil in water is also due to the existence of electrical double layers surrounding the particles, but unfortunately for the colloidal speculations on "emulsoids" Powis has shown that the P.D. surrounding droplets of oil is destroyed by the same low concentration of salts as the P.D. of "suspensoids," and that in the case of emulsions of oil in water the effective ion of the salt has the opposite sign of charge from that of the oil drop.[3]

All amino-acids form crystalloidal solutions but some, like alanine, are very soluble while others, like tyrosine, are sparingly soluble in water. Similar differences must exist between proteins, according to the nature and linkage of the amino-acids of which they are composed. When the forces of attraction between the molecules of the solute and the solvent become smaller than the forces of attraction between the molecules of the solute (or of certain groups like hydrocarbons) for each other, aggregates of molecules will be formed. If it happens that electrical double layers are formed around each nascent aggregate, no flocculation need occur, the aggregates forming stable suspensions. Flocculation of such suspensions can be brought about when the P.D. of the double layer surrounding each particle is lowered below a critical limit by the addition of electrolytes. It is, however, quite possible that the addition of salt may increase the forces of attraction between the solute and water. It may also happen, as was demonstrated by Northrop and De Kruif, that a salt may diminish the forces of cohesion between the micellæ and in that case

[3] Powis, F., *Z. physik. Chem.*, 1914-15, lxxxix, 186.

no flocculation of aggregates will occur even if the salt annihilates the P.D. between particle and water.[4] In view of all these possibilities it is necessary actually to measure the P.D. between protein particles and water before any decision can be reached whether or not proteins are kept in solutions by electrical double layers or by those forces which determine the solution of crystalloids. The writer has measured the influence of electrolytes on the P.D. of the electrical double layer surrounding protein particles to separate the influence of these forces from the influence of forces which determine the stability of crystalloidal solutions and it is the intention of this paper to give the results of these measurements. The question concerning the origin of these electrical double layers will be discussed in a subsequent paper.

II.

Three sets of experiments were made: namely, first, with collodion particles coated with gelatin; second, with casein particles containing no collodion; and third, with particles of denatured egg albumin.

For the first set of experiments, with collodion particles coated with gelatin, the same collodion particles were used as in the preceding paper.[5] To a thick suspension of these particles was added enough isoelectric gelatin to make a 1 per cent gelatin solution. The water used for the solution had a pH of 4.7; *i.e.*, the pH of the isoelectric point of gelatin. The collodion particles remained in the solution over night. The next day the suspension in gelatin was heated to about 40°C. to make sure that the gelatin was completely liquefied, and the collodion particles were centrifuged out from the gelatin solution while the latter was still warm. The thick sediment of collodion particles which was centrifuged out was suspended in 50 cc. of water of pH 4.7 and kept as a stock suspension. This stock suspension was too concentrated for microscopic measurement of the migration in an electric field and a few drops of the stock suspension were usually put into 50 cc. of a solution of an electrolyte, shaken up, and left standing for 30 minutes at about 24°C. This suspension was then used for microscopic measurement of the velocity in an electric field.

[4] Northrop, J. H., and De Kruif, P. H., *J. Gen. Physiol.*, 1921–22, iv, 639, 655.

[5] Loeb, J., *J. Gen. Physiol.*, 1922–23, v, 109.

In the first sets of experiments the gelatin-collodion particles were suspended in various concentrations of HCl, H_2SO_4, NaOH, and $Ba(OH)_2$, and Fig. 1 gives the cataphoretic P.D. as calculated from the mobility measurements. The abscissæ are the equivalent concentrations of acid and alkali. On account of the Donnan equilibrium the pH of the surface film of gelatin on the collodion particles was higher than that of the acid solution used. The ordinates are

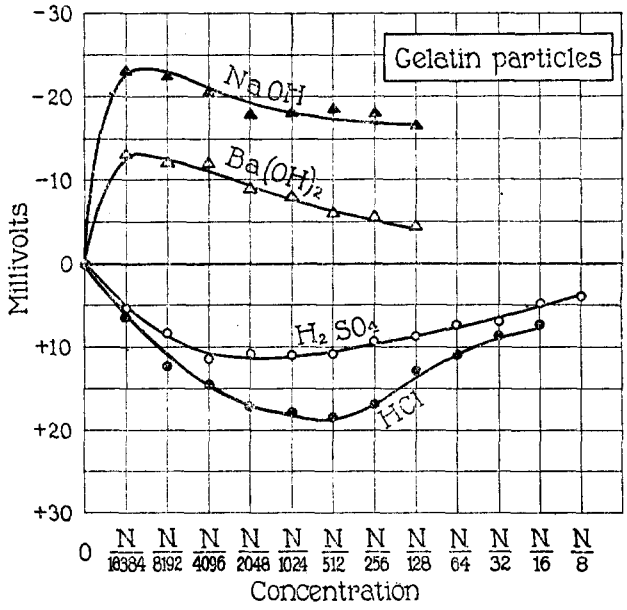

FIG. 1. Influence of acids and alkalies on the cataphoretic P.D. of collodion particles coated with isoelectric gelatin. Abscissæ are the normality of acids or alkalies in solution; ordinates are the cataphoretic P. D. of the particles in millivolts. The ordinates are above the zero line when the particles are negatively charged, and below when they are positively charged.

the P.D. in millivolts; when the particles were negatively charged the ordinates were plotted above the zero line, so as to make the curves comparable to the curves for the P.D. of the collodion particles free from protein published in the preceding paper. When the collodion-gelatin particles were positively charged, the ordinates were plotted below the zero line.

Fig. 1 shows that at the isoelectric point the P.D. was zero, that in

acid the particles were positively charged, and in alkali negatively charged. This was to be expected. The new part in our experiments is the variation of the P.D. with the concentration of acid or alkali used. In H_2SO_4 the P.D. curve reaches a maximum at a concentration of about N/4,096 and then falls slowly. This agrees approximately with the membrane potentials between H_2SO_4 and gelatin sulfate solutions, as shown on page 129 of the writer's book. The absolute values of the P.D. are, however, lower in the cataphoretic P.D. curve in this paper than in the membrane potentials. This cannot be explained since we know nothing of the concentration of the gelatin in the surface film on the collodion particles.

The curve for HCl in Fig. 1 shows that the P.D. is higher than in the case of H_2SO_4. If the Donnan equilibrium were the cause of the cataphoretic P.D. of the gelatin-collodion particles, the ratio of the values of the curves should be as 2:3. This is approximately the case. Thus at N/1,024 the P.D. for gelatin chloride was 18 and for gelatin sulfate 11 millivolts. It must, however, be remembered that the values for the cataphoretic P.D. are liable to have an error of $\pm$ 2 millivolts.

In the case of NaOH and $Ba(OH)_2$ the gelatin-collodion particles are negatively charged and the charge is lower in the case of $Ba(OH)_2$ than in the case of NaOH.

The character of these P.D. curves for acid and alkali has a great theoretical significance since it seems to eliminate one possible source for the cataphoretic P.D. It had been suggested that colloidal micellæ migrate in the galvanic field not on account of an electrical double layer surrounding them but on account of the drag on the colloidal ions contained in the micella. If this were the case, the P.D. curves for NaOH or $Ba(OH)_2$ should be interpreted to mean that in a concentration of M/16,000 NaOH or $Ba(OH)_2$ the ionization of Na gelatinate was a maximum and that its ionization was repressed at higher concentrations of these alkalies, and that the ionization of gelatin chloride was a maximum in M/512 HCl and was repressed at higher acid concentrations. Both assumptions would be contrary to fact.[6] This leaves only one possible explanation for the migration of the gelatin

[6] Loeb, J., Proteins and the theory of colloidal behavior, New York and London, 1922, 116–119.

micellæ in an electric field; namely, that it must be due to the formation of an electrical double layer between particles and surrounding aqueous solution.

The stock suspension of gelatin-coated particles had a pH of 4.7, and several drops of this suspension were put into 50 cc. of different concentrations of a solution of electrolytes, NaCl, Na_2SO_4, $Na_4Fe(CN)_6$, $CaCl_2$, and $LaCl_3$, all of a pH of 4.7, and the sign and rate of migration were observed. In this case it is very essential that the pH of the solution should be exactly 4.7, since a slight deviation from this pH will cause a migration of the particles. Without the addition of salt, the P.D. of the particles was found in the five series to be −1.5, −1.7, +1.0, −3.0, −1.8 millivolts respectively; in other

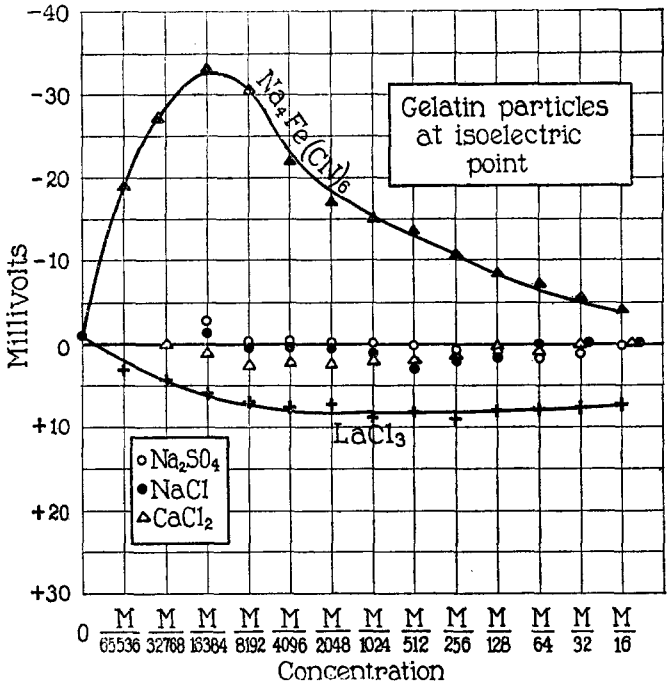

FIG. 2. Influence of different salts on the cataphoretic P. D. of gelatin-collodion particles at pH 4.7 (isoelectric point). Without salts the particles are not charged. In $Na_4Fe(CN)_6$ the particles are negatively charged; in $LaCl_3$ they are positively charged. The effect of NaCl, Na_2SO_4, and $CaCl_2$ is scarcely noticeable, except that in $CaCl_2$ the particles are slightly more positive than in either NaCl or Na_2SO_4.

words, there was practically no migration of the particles at the isoelectric point. This agrees with the results of the previous observers.

In our experiments on anomalous osmosis the conclusion was reached that the presence of NaCl, Na_2SO_4, and $CaCl_2$ leaves isoelectric gelatin particles uncharged. Fig. 2 shows that the gelatin-coated collodion particles have possibly a very minute positive charge in the presence of $CaCl_2$ which is lacking in the case of Na_2SO_4. It is very small, and might be due to experimental error; it is, however, too persistent to be discarded in this way. $LaCl_3$, however, gives the isoelectric gelatin-collodion particles a positive charge and $Na_4Fe(CN)_6$ gives them a negative charge. The same effect of these two salts was observed in the case of anomalous osmosis through gelatin-coated collodion membranes.[7] The influence of $LaCl_3$ and of $Na_4Fe(CN)_6$ on the cataphoretic P.D. of gelatin particles is much greater than on the membrane potentials of isoelectric gelatin. In the latter case it was only a few millivolts while $Na_4Fe(CN)_6$ raised the cataphoretic P.D. of isoelectric gelatin more than 30 millivolts.

At pH 4.0 the gelatin-collodion particles had a cataphoretic P.D. of about 13 millivolts, the particles being positively charged. $LaCl_3$, $CaCl_2$, and NaCl depress the P.D. to the same extent at the same concentration of Cl ions (within the limits of experimental accuracy) as is shown by the curves in Fig. 3. Na_2SO_4 should depress the P.D. more powerfully than NaCl, and this is shown in Fig. 3 to be true. $Na_4Fe(CN)_6$, however, makes the particles negative at a very low concentration, and at a concentration of M/2,048 the P.D. is over 20 millivolts.

Fig. 4 gives the influence of the four salts NaCl, $CaCl_2$, $LaCl_3$, and Na_2SO_4 on the P.D. of gelatin-collodion particles at pH 3.0. The effect of the first three salts is about the same while Na_2SO_4 has a much stronger depressing effect.

At pH 5.8 the cataphoretic P.D. was about 14 millivolts without the addition of salts, the gelatin particles being negatively charged (Fig. 5). In this case they should be influenced by salts in the same way as the collodion particles not treated with gelatin, since such collodion particles are also negatively charged. While, however, NaCl, Na_2SO_4, and $Na_4Fe(CN)_6$ raise the P.D. of collodion particles not

[7] Loeb, J., *J. Gen. Physiol.*, 1921–22, iv, 463.

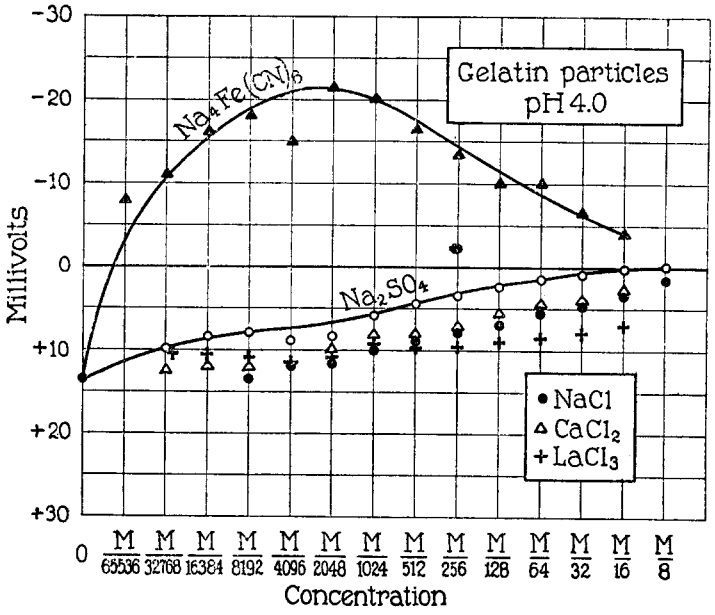

FIG. 3. Influence of salts on the cataphoretic P. D. of gelatin-collodion particles at pH 4.0. In $Na_4Fe(CN)_6$ the particles are negatively, in the other salts positively charged. In Na_2SO_4 the particles are charged less than in NaCl, $CaCl_2$, or $LaCl_3$.

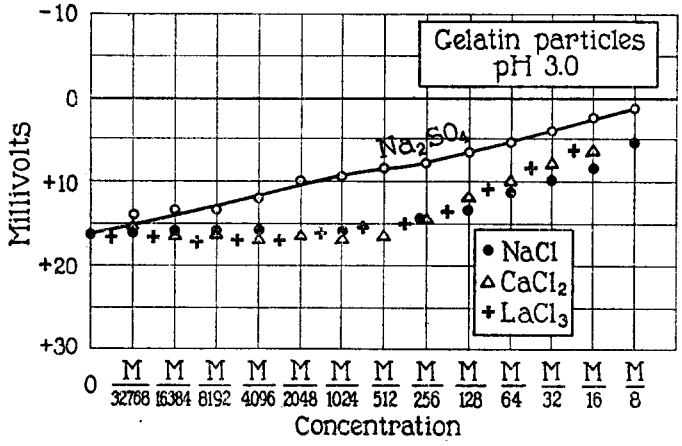

FIG. 4. Influence of salts on cataphoretic charges of gelatin-collodion particles at pH 3.0. The particles are positively charged.

treated with gelatin from about 20 to 30 millivolts to about 60 to 70 millivolts, particles coated with gelatin were practically not influenced by NaCl and Na_2SO_4, while $Na_4Fe(CN)_6$ made the particles more negative. The depressing effect of $CaCl_2$ is slightly higher than should be expected on the basis of the Donnan effect alone. $LaCl_3$ not only depresses the P.D., but actually causes the collodion-gelatin particles to assume a positive charge when the concentration of $LaCl_3$ rises above M/16,384.

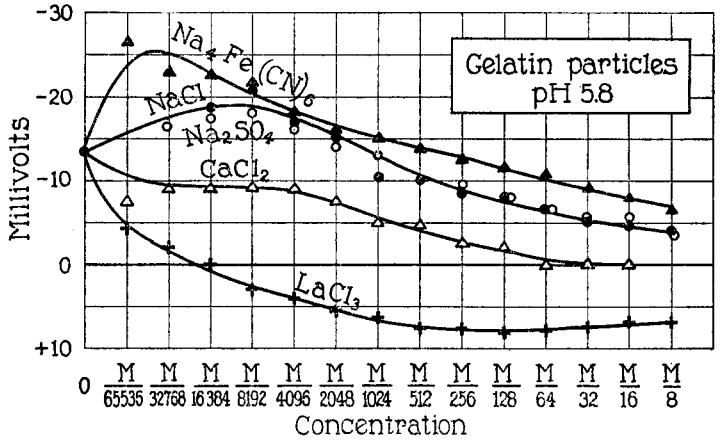

FIG. 5. Influence of salts on the cataphoretic charge of gelatin-collodion particles at pH 5.8. $LaCl_3$ reverses the negative charge of the particles.

III.

These experiments were open to the objection that the collodion beneath the layer of gelatin might influence the P.D. This objection is justified since it is uncertain whether or not the layer of gelatin on the surface of the collodion particles is continuous—there may be spots on the surface where the gelatin is lacking. It is also uncertain how thick the layer of gelatin on the surface of the collodion particles is. It was, therefore, advisable to make experiments with another genuine protein, which can easily be obtained in the form of minute granules, without the aid of some foreign material such as collodion. Such material was available in the form of isoelectric casein, which if properly prepared can be obtained in very minute

solid particles, which dissolve only very slowly in acid solution. In alkaline solution, *i.e.* at a pH above 7.0, they dissolve rapidly but it is not necessary for our purpose to experiment at a pH above 5.8. Since the isoelectric point of casein is practically identical with that of gelatin, *i.e.* pH 4.7, all the mobility measurements made with gelatin-coated collodion particles could thus be repeated with casein particles free from collodion. The results obtained with casein particles were almost identical with those obtained with gelatin-coated collodion particles.

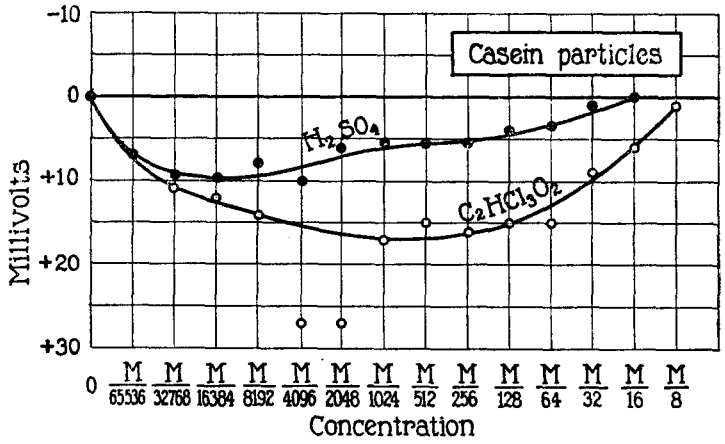

FIG. 6. Influence of trichloroacetic and sulfuric acids on the cataphoretic P.D. of casein particles.

The method of evaluating the cataphoretic P.D. of the casein particles was the same as that used for evaluating the cataphoretic P.D. of the gelatin-coated particles. Fig. 6 gives the effects of different concentrations of trichloroacetic and sulfuric acids on the cataphoretic P.D. of originally isoelectric particles of casein. Trichloroacetic acid was selected because casein is practically as insoluble in this acid as in sulfuric acid. At pH 4.7 the P.D. of the casein particles was zero. It increased with increasing concentrations of acid until it reached a maximum at a molecular concentration of between M/4,096 and M/256, and then diminished again with increasing concentration of acid. The particles were positively charged.

Fig. 7 shows the influence of five salts, $LaCl_3$, $CaCl_2$, NaCl, Na_2SO_4,

and $Na_4Fe(CN)_6$ on the cataphoretic P.D. of the casein particles at the isoelectric point; *i.e.*, pH 4.7. As was to be expected the $LaCl_3$ causes the isoelectric casein particles to be positively charged, and $Na_4Fe(CN)_6$ causes them to be negatively charged. Fig. 7 shows also that the particles are slightly more negative in the presence of Na_2SO_4 than in the case of NaCl, and more so in this case than in that

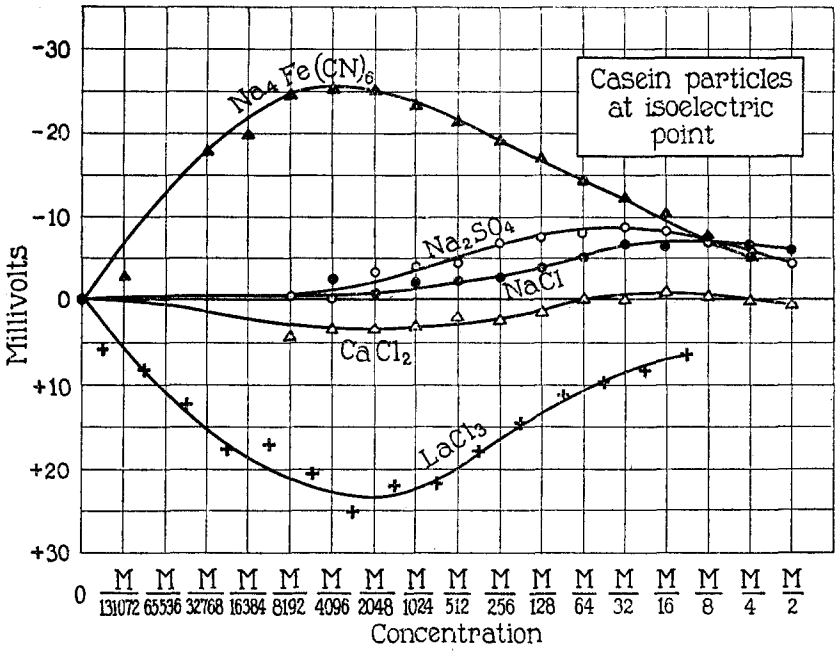

FIG. 7. Influence of salts on the cataphoretic P. D. of casein particles at pH 4.7 (isoelectric point). Without salts the particles are not charged. In the presence of $Na_4Fe(CN)_6$ they are negatively, and in $LaCl_3$ they are positively charged. In Na_2SO_4 the particles are slightly negatively, in $CaCl_2$ slightly positively charged.

of $CaCl_2$. The latter salt may make the casein particles even slightly positive. The effects of these three salts, though slight, cannot be ascribed to an error.

The next group of measurements was made at pH 4.0 (Fig. 8). The acid used to bring the particles to this pH was HCl and hence the casein salt formed was casein chloride. The cataphoretic P.D. of the casein particles was about 14 millivolts, in the absence of salts,

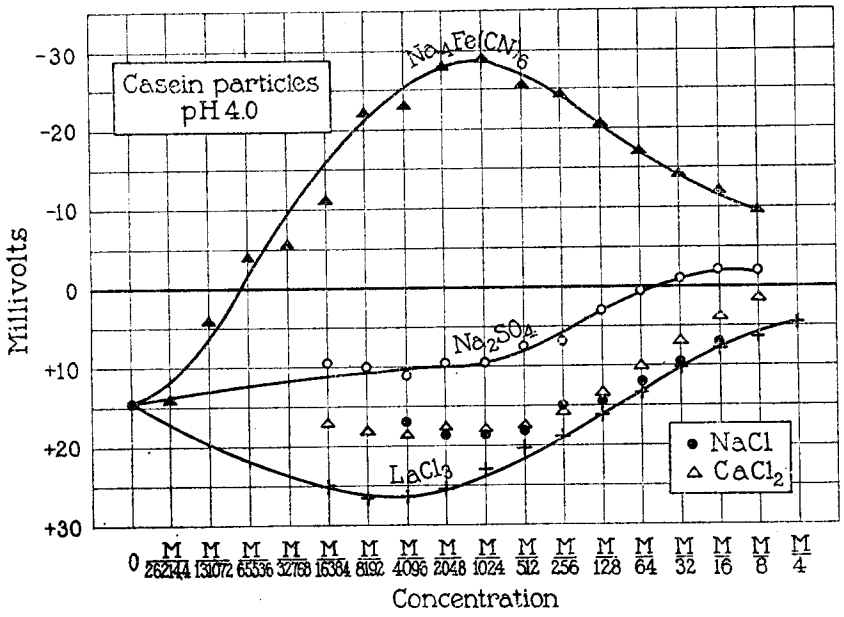

FIG. 8. Influence of salts on the cataphoretic P. D. of casein particles at pH 4.0.

the particles being positively charged. Na_2SO_4 diminished the P.D. more than NaCl, $CaCl_2$, or $LaCl_3$. $Na_4Fe(CN)_6$ reverses the sign of charge of the protein particles in concentrations above M/65,000.

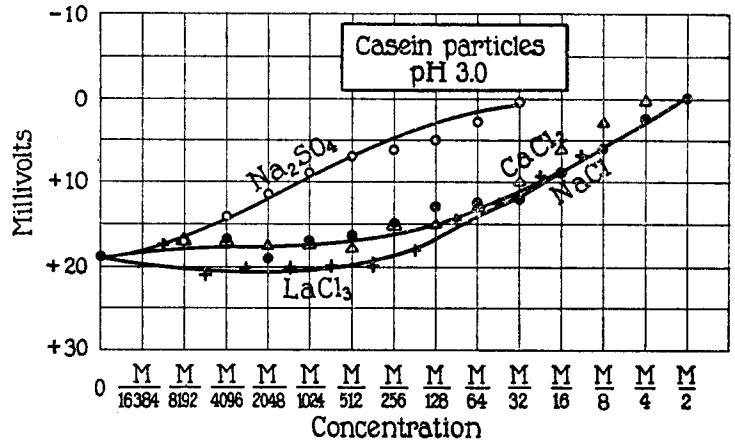

FIG. 9. Influence of salts on the cataphoretic P. D. of casein particles at pH 3.0.

Fig. 9 shows the effect of $LaCl_3$, $CaCl_2$, NaCl, and Na_2SO_4 on the cataphoretic P.D. of casein particles at pH 3.0. The acid used to produce this pH was again HCl.

At pH 5.8 the particles of casein should be negatively charged. Fig. 10 shows that this is the case since without salt the P.D. is about

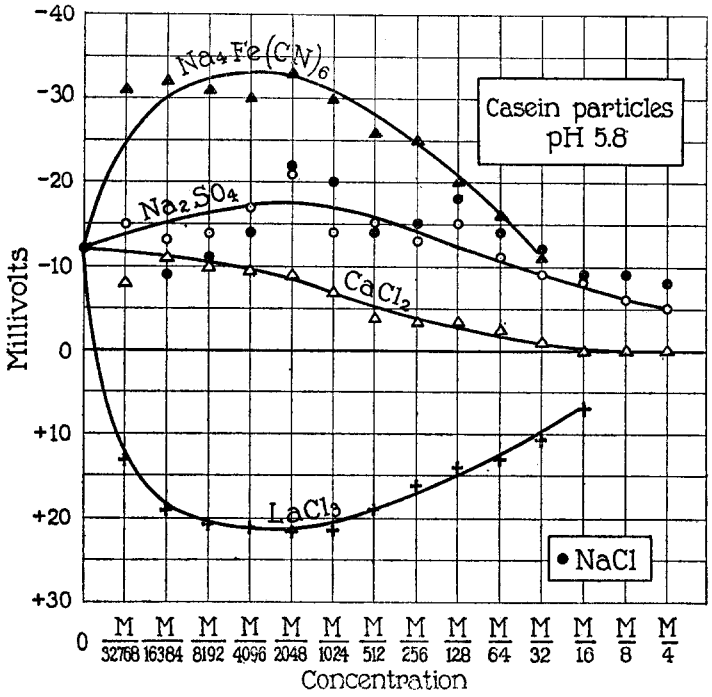

FIG. 10. Influence of salts on the cataphoretic charge of casein particles at pH 5.8. Without salts the particles are negatively charged. $LaCl_3$ reverses the sign of charge.

12 millivolts, the particles being negatively charged. NaCl and Na_2SO_4 increase the negative charge of the particles but slightly, while $Na_4Fe(CN)_6$ increases it markedly. $CaCl_2$ depresses the charge and $LaCl_3$ reverses the sign of charge.

IV.

It seemed advisable to investigate also the influence of salts on the cataphoretic P.D. of denatured crystalline egg albumin. Denatured

egg albumin was prepared by heating a 1 per cent solution of crystalline egg albumin of pH 4.8 to 90°C. allowing the coagulated particles to settle. The sediment was then ground up in a mortar with a small amount of water to a milky suspension. 4 drops of this suspension were then added to 50 cc. of the various solutions used. This latter suspension was always allowed to stand 20 minutes at room temperature in the solution before the mobility measurements in Northrop's apparatus were made. It was found that the influence of electrolytes on the cataphoretic P.D. of denatured egg albumin was about the same as on casein and gelatin particles, as is shown in Figs. 11 to 15.

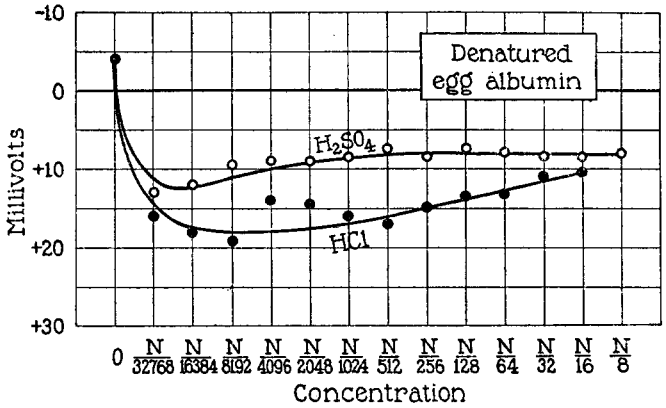

FIG. 11. Influence of HCl and H_2SO_4 on the cataphoretic P.D. of particles of denatured egg albumin.

Fig. 11 gives the influence of HCl and H_2SO_4 on the cataphoretic P.D. of particles of denatured egg albumin. The influence of the two acids corresponds almost to that to be expected on the basis of the Donnan equilibrium.

Fig. 12 shows the influence of the five salts, NaCl, Na_2SO_4, $CaCl_2$, $LaCl_3$, and $Na_4Fe(CN)_6$ on the cataphoretic P.D. of almost isoelectric egg albumin (pH 5.0 instead of 4.8). The particles are uncharged and NaCl, Na_2SO_4, and $CaCl_2$ have almost no influence on the P.D., while $LaCl_3$ acts like acid and $Na_4Fe(CN)_6$ like alkali.

At pH 4.0 (Fig. 13) the particles of egg albumin have a positive charge and the P.D. is about 20 millivolts. $Na_4Fe(CN)_6$ reverses the charge at a concentration of M/16,000, while $LaCl_3$ increases the

charge slightly. NaCl and $CaCl_2$ have only a depressing effect due to the Cl ions, and Na_2SO_4 has a much stronger depressing effect. Na_2SO_4 does not reverse the sign of charge as does $Na_4Fe(CN)_6$.

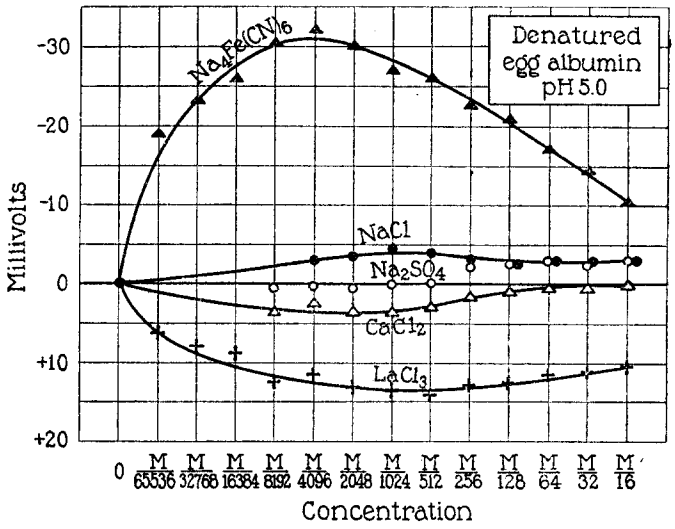

FIG. 12. Influence of salts on the cataphoretic P.D. of particles of denatured egg albumin near the isoelectric point.

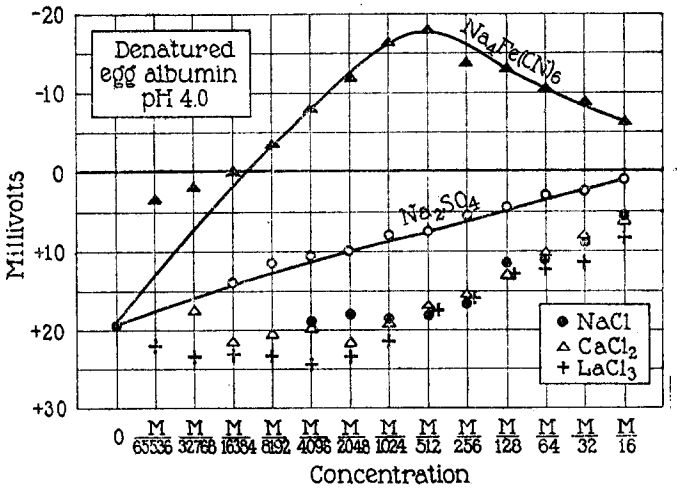

FIG. 13. Influence of salts on the cataphoretic P.D. of particles of denatured egg albumin at pH 4.0.

Fig. 14 shows the effects of NaCl, $CaCl_2$, $LaCl_3$, and Na_2SO_4 on the P.D. of egg albumin at pH 3.0, and Fig. 15 shows the effects of salts on the P.D. of Na albuminate at pH 5.8. In this latter case the protein

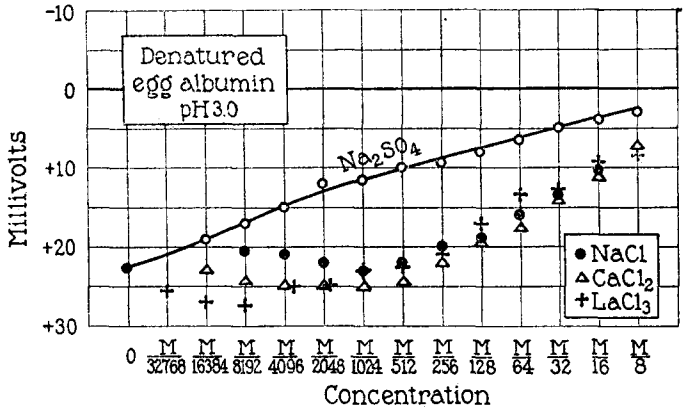

FIG. 14. Influence of salts on the cataphoretic P.D. of particles of denatured egg albumin at pH 3.0.

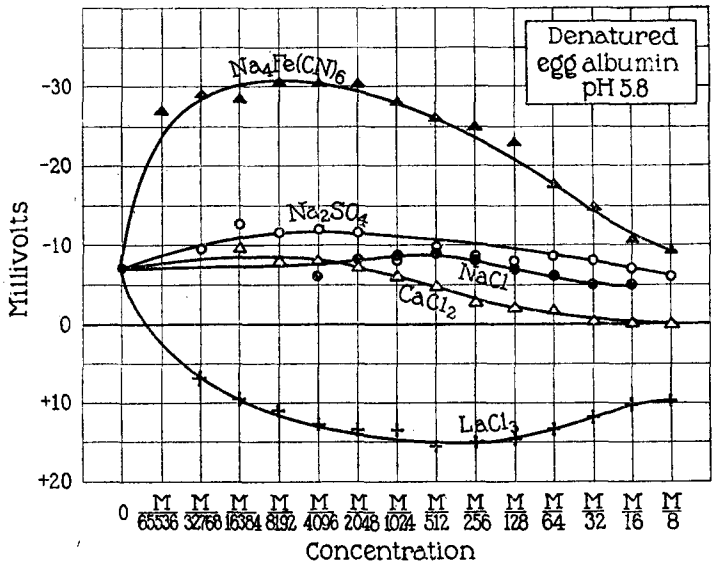

FIG. 15. Influence of salts on the P.D. of particles of denatured egg albumin at pH 5.8.

has a negative charge and the P.D. was about 8 millivolts. NaCl, Na_2SO_4, and $CaCl_2$ had practically only a depressing effect, which was greater in the case of $CaCl_2$ than in the case of NaCl or Na_2SO_4. $LaCl_3$, however, reversed the sign of charge making the protein particles strongly positive.

V.

SUMMARY AND CONCLUSIONS.

1. This paper gives measurements of the influence of various electrolytes on the cataphoretic P.D. of particles of collodion coated with gelatin, of particles of casein, and of particles of boiled egg albumin in water at different pH. The influence of the same electrolyte was about the same in all three proteins.

2. It was found that the salts can be divided into two groups according to their effect on the P.D. at the isoelectric point. The salts of the first group including salts of the type of NaCl, $CaCl_2$, and Na_2SO_4 affect the P.D. of proteins at the isoelectric point but little; the second group includes salts with a trivalent or tetravalent ion such as $LaCl_3$ or $Na_4Fe(CN)_6$. These latter salts produce a high P.D. on the isoelectric particles, $LaCl_3$ making them positively and $Na_4Fe(CN)_6$ making them negatively charged. This difference in the action of the two groups of salts agrees with the observations on the effect of the same salts on the anomalous osmosis through collodion membranes coated with gelatin.[7]

3. At pH 4.0 the three proteins have a positive cataphoretic charge which is increased by $LaCl_3$ but not by NaCl or $CaCl_2$, and which is reversed by $Na_4Fe(CN)_6$, the latter salt making the cataphoretic charge of the particles strongly negative.

4. At pH 5.8 the protein particles have a negative cataphoretic charge which is strongly increased by $Na_4Fe(CN)_6$ but practically not at all by Na_2SO_4 or NaCl, and which is reversed by $LaCl_3$, the latter salt making the cataphoretic charge of the particles strongly positive.

5. The fact that electrolytes affect the cataphoretic P.D. of protein particles in the same way, no matter whether the protein is denatured egg albumin or a genuine protein like gelatin, furnishes proof that the solutions of genuine proteins such as crystalline egg albumin or gelatin

are not diaphasic systems, since we shall show in a subsequent paper that proteins insoluble in water, *e.g.* denatured egg albumin, are precipitated when the cataphoretic P.D. falls below a certain critical value, while water-soluble proteins, *e.g.* genuine crystalline egg albumin or gelatin, stay in solution even if the P.D. of the particles falls below the critical P.D.

The mobility measurements mentioned in this paper were made by Mr. M. Kunitz.