

edge of any approximate values for the radii; and this constitutes one of the chief reasons for expecting these tables to prove generally serviceable.

The authors deserve the thanks of optical computers further, in particular, for their care in testing results by trigonometrical calculations. Judging from more than a hundred such verifications, they inform us, the small errors in the approximate values of spherical aberration occur only in the fourth decimal place, so that they would hardly influence the specifications to be given to the mechanician. The data in the first tables run to three decimal places.

Of major significance are the graphs, pages 80 and 81, showing the performance of typical lenses of the various types at different apertures. Group A makes quite the best showing. The final page, with some general conclusions, may well be read first.

American readers will have noticed already, from certain reports published by the Bureau of Standards, that projects not wholly dissimilar to this have been under consideration, and are already partially realized, for lightening the arduous labor of finding satisfactory first approximations in definite types of lens design.

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SPECIAL ARTICLES

ELECTROLYTES AND COLLOIDS

THE effect of ions on the physical properties of proteins is one of the most interesting chapters of colloid chemistry. The work on this topic quoted in the textbooks of colloid chemistry suffers from two sources of error, namely, first, that the effect of the hydrogen ion concentration is generally ignored, and second, that the effect of the nature of ions on the physical properties of proteins is often ascertained in the presence of an excess of an electrolyte. Proteins are amphoteric electrolytes and therefore occur in three states according to the hydrogen ion concentration, namely as: (1) protein, free from ionogenic impurities, (isoelectric protein); (2) metal proteinates, *e. g.*, sodium proteinate or cal-

cium proteinate, etc.; and (3) protein acids, *e. g.*, protein chloride or protein sulfate, etc. For gelatin the hydrogen ion concentration defining the isoelectric point is, as Michaelis¹ first showed, about 2×10^{-5} N (or in Sørensen's logarithmic symbol $\text{pH} = 4.7$). At this hydrogen ion concentration gelatin can practically combine with neither anions nor cations of an electrolyte. When the hydrogen ion concentration becomes lower than 2×10^{-5} , *e. g.*, through the addition of NaOH, part of the isoelectric gelatin is transformed into sodium gelatinate, and the relative amount of isoelectric or non-ionogenic gelatin transformed into sodium gelatinate increases with the diminution of the hydrogen ion concentration. Sodium gelatinate can exchange its cation with the cation of neutral salts but is not (or practically not) affected by the anion of a neutral salt. When we raise the hydrogen ion concentration of gelatin solutions above that of the isoelectric point, *e. g.*, by adding HCl, isoelectric gelatin will be transformed into gelatin chloride and the transformation will become the more complete the higher the hydrogen ion concentration, until finally all the isoelectric gelatin is transformed into gelatin chloride. The gelatin-acid salts can exchange their anion with the anion of other salts but are not (or practically not) affected by the cation of other salts.²

While isoelectric gelatin has a minimal osmotic pressure, a minimal power of swelling, a minimal viscosity, a minimal transparency, a minimal alcohol number, etc., gelatin salts, *e. g.*, sodium gelatinate or gelatin chloride, have a high osmotic pressure, a high power of swelling, a high viscosity, etc. The writer has been able to show by volumetric analysis that the osmotic pressure, the power of swelling, etc., of gelatin increase with the relative amount of isoelectric gelatin transformed into gelatin salt.³ The physical properties of gelatin, *e. g.*, its

¹ Michaelis, L., "Die Wasserstoffionenkonzentration," Berlin, 1914.

² Loeb, J., *J. Gen. Physiol.*, 1918-19, I., 39, 237.

³ Loeb, J., *J. Gen. Physiol.*, 1918-19, I., 237, 363, 483, 559.

osmotic pressure, depend therefore not only upon the concentration of the gelatin in solution but also upon the hydrogen ion concentration.

Colloid chemists usually state only the amount of acid added to a protein without measuring the hydrogen ion concentration of their protein solution. The effect of the addition of the same amount of acid upon the chemical and physical properties of gelatin is entirely different according to the hydrogen ion concentration of the gelatin used. When a slight amount of acid is added to isoelectric gelatin it will increase its osmotic pressure while the same amount of acid if added to gelatin with a $\text{pH}=3.3$ or to neutral gelatin ($\text{pH}=7.0$) will diminish its osmotic pressure. Since the hydrogen ion concentration of commercial gelatin varies and since, moreover, the combining power of different acids with gelatin varies also,⁴ the results obtained by the addition of electrolytes without measurement of the hydrogen ion concentration are irregular and confusing.

In addition, the properties of gelatin salts depend upon at least two more variables, namely, the nature of the ion in combination with the gelatin and the concentration of electrolyte present. When we transform 1 per cent. solutions of isoelectric gelatin into sodium gelatinate and calcium gelatinate both possessing the same hydrogen ion concentration (*e. g.*, 10^{-9}) the sodium gelatinate has an osmotic pressure more than twice as great as the calcium gelatinate. This difference is not due to a difference in the degree of electrolytic dissociation since both solutions have the same conductivity.⁵ When we add increasing quantities of neutral salts or alkalies to the two solutions the osmotic pressure is depressed in both solutions and if enough is added the osmotic pressure falls to almost zero in both solutions. (If we add acid, the same will occur but for another reason, the metal gelatinate being brought to the isoelectric point, and, by addition of more

acid, being transformed into gelatin-acid salts.)

The same difference as between sodium and calcium gelatinate exists between gelatin chloride and gelatin sulfate⁴ and this difference is also obliterated when neutral salt or acid is added to the solution. (The addition of an excess of alkali would transform the gelatin acid into isoelectric gelatin and finally into metal gelatinate.)

If we wish to investigate the specific effect of different ions on the physical properties of gelatin (or of proteins in general) it is therefore necessary to avoid an excess of electrolytes. The writer proceeds in the following way. Finely granulated (commercial) gelatin is brought to the isoelectric point by the method described in the writer's previous publications. Isoelectric gelatin if properly washed will lose its ionogenic impurities. Just enough acid or alkali is then added to 1 gm. of isoelectric gelatin to produce a gelatin salt (either gelatin acid or metal gelatinate) of the desired hydrogen ion concentration. Since there exists an equilibrium between free acid (or free alkali) gelatin salt and isoelectric (non-ionogenic) gelatin two solutions of metal gelatinate (*e. g.*, Na gelatinate and Ca gelatinate) each containing 1 gm. of isoelectric gelatin and each possessing the same hydrogen ion concentration contain the same proportion of metal gelatinate and non-ionogenic gelatin. Differences in the physical properties of these two solutions may be ascribed to differences in the effect of the metal ion in combination with the gelatin. The same is true for solutions of gelatin chloride and gelatin sulfate of the same hydrogen ion concentration if prepared from isoelectric gelatin of the same concentration. If this procedure is not followed, erroneous results will be obtained such as are found in the textbooks of colloid chemistry. Thus it is generally stated that acids and alkalies increase the osmotic pressure of gelatin while neutral salts depress it. This statement is entirely wrong and due to the fact that the experimenter responsible for this statement did not work with gelatin

⁴ Loeb, J., *J. Gen. Physiol.*, 1918-19, I., 559.

⁵ Loeb, J., *J. Gen. Physiol.*, 1918-19, I., 483.

solutions standardized according to the method just described. Correct and constant results can only be obtained if such a method of standardization is used.

Another error which permeates the literature of colloid chemistry is due to Hofmeister's experiments on the influence of different ions on the swelling of gelatin. Hofmeister's experiments were all made in the presence of an excess of electrolyte, in which the specific effect of different ions can no longer be recognized. When we prepare sodium and calcium gelatinates or gelatin chloride and gelatin sulfate according to the writer's method and put them into distilled water we find that the sodium gelatinate swells considerably more than the calcium gelatinate and that the gelatin chloride swells considerably more than the gelatin sulfate of the same concentration of isoelectric gelatin and of hydrogen ions. If, however, we add neutral salt or alkali to the two solutions of metal gelatinates or neutral salts or acid to the solutions of gelatin chloride and gelatin sulfate the differences in swelling disappear since in all cases the swelling is repressed. It is only necessary to add enough electrolyte so as to make the solution M/4 or even less to completely mask the differences. The writer feels therefore justified in stating that if we wish to compare the effect of different ions on the physical properties of gelatin we must avoid the error of adding an excess of electrolyte to the solution.

A writer⁶ in *Nature* has raised the objection that Sørensen's experiments on the osmotic pressure of egg albumin were done in the presence of ammonium sulfate, but he overlooks the fact that Sørensen's experiments⁷ were not concerned with the comparison of the effect of different ions on the osmotic properties of egg albumin. If it had been Sørensen's intention to compare the osmotic pressure of albumin chloride with that of albumin sulfate or of sodium albuminate with that of calcium albuminate he

would have found it necessary to take cognizance of the fact that the specific effects of different ions on the physical properties of gelatin (or possibly of proteins in general) are repressed in the presence of an excess of electrolyte. As far as the writer is aware there is no disagreement between his results and views and those of Sørensen, though there is a difference in the method employed and the nature of the protein used.

The writer's recent experiments, seem to indicate that the specific influence of the nature of ions as well as the depressing effect of an excess of electrolyte on the physical properties of colloids are connected with the electrification of water, and that this connection seems to be the same in the case of crystalloidal and of colloidal solutions of electrolytes. Since it would exceed the limits of this note to discuss these observations, the reader interested in this feature of the problem is referred to the writer's publications on the subject in the current numbers of the *Journal of General Physiology* and the *Proceedings of the National Academy of Sciences*.⁸

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II

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⁶ *Nature*, 1919, CIV. (September 4), 15.

⁷ Sørensen, S. P. L., *Compt. rend. trav. Lab. Carlsberg*, 1917, XII.

⁸ Loeb, J., *J. Gen. Physiol.*, 1918-19, I., 717; 1919-20, II., 87.