by the equation, $HSCSN_3 = HSCN + S + N_2$. The solid product finally formed consists of polymerized thiocyanic acid and free sulfur.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

DENSITY AND HYDRATION IN GELATIN SOLS[1]

BY THE SVEDBERG AND BRUNO A. STEIN

RECEIVED AUGUST 11, 1923

Introductory and Theoretical

It is known that in the case of true solution and in colloidal solutions there is more or less combination between the solute or the particles and the solvent or dispersing phase.

Nägeli long ago advanced the idea that solution was a process in which the material was surrounded by a shell of water. Pauli[2] states, "Crystalloids are said to be hydrated (or, in general, solvated) in solution when water is attached to the dissolved molecules in a stoichiometric proportion. In some instances this hydration is sharply defined (as for sulfuric acid and ferric chloride), but in other cases the hydration is variable and shows a continual alteration with dilution and with change of temperature. We can describe such phenomena with more accuracy as addition of water (or formation of envelopes) by the particles, ..."

"Such an addition of the medium occurs on the particles of many colloids, and is described as hydration. . . . The indications of hydration of a disperse phase are a disproportionately great viscosity of the solution, a decreased activity of the movement of the particles as displayed in diffusion or in an electric field, and an alteration in volume or density in the direction of compression of the medium." Zsigmondy[3] assumes that a density increase must be due to a compression of the particle by its water layer. A contraction in volume when gelatin is dissolved in water is then an evidence of hydration. The varying amount of water in gelatinous coagula shows hydration. Zsigmondy[4] states that egg white and gelatin must have thicker layers of water than the non-soluble gold and that this assumption probably explains the stability of the former to addition of electrolytes. This exemplifies sols of the hydrophile and hydrophobe type. This author feels that this stability is due to the film of water rather than to the dispersion size of gelatin and gold. Remy also[5] ascribes a shell of water (Wasserhülle) to the ions of salts in solution.

A high degree of hydration corresponds to a high viscosity in the sol according to Pauli[6] and Hatschek.[7] At the iso-electric point of gelatin, at *P*H about 4.7, a mini-

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[1] This paper constitutes the major portion of a thesis submitted by Bruno A. Stein in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

[2] Pauli, "Colloid Chemistry of the Proteins," P. Blakiston's Son and Co., Philadelphia, **1922**, p. 10.

[3] Zsigmondy, "Kolloid Chemie," Otto Spamer, Leipzig, **1920**, 3rd ed., p. 99.

[4] Ref. 3, pp. 97–100.

[5] Remy, *Z. physik. Chem.*, **89**, 467 (1915).

[6] Pauli, *ibid.*, **89**, 529 (1915).

[7] Hatschek, "Introduction to Physics and Chemistry of Colloids," J. and A. Churchill, London, **1922**, 4th ed., p. 84.

mum viscosity is observed by Loeb, and it therefore would be also a minimum of hydration.[8] At PH 3.0–3.2 there is a maximum hydration according to the same authority.

As stated above, Pauli explained the decrease in volume, or increase in density, since the two are reciprocal functions, when proteins are dissolved, by assuming hydration of the particles. We picture the particle surrounded by a shell of highly compressed water. Measurements of the density of gelatin sols should give a measure of the degree of hydration. It was thought that if density determinations over a range of Sörensen values should show a maximum for acids at PH 3.2, which corresponds to the point of maximum viscosity, then Pauli's hydration theory would be further verified.

Pauli and Handovsky have shown that salts in general have a depressing effect upon the viscosity of protein sols. This is also true for some organic substances. It was thus hoped to get at the hydration by means of variations in density with different concentrations of acids, salts, and non-electrolytes.

Experimental Part

Approximately 2 N, N, 0.1 N, and 0.001 N solutions of acids were prepared (it was not necessary to have the normality absolutely exact since the Sörensen values were determined later with the hydrogen electrode, these values being tabulated in Table II). Salt solutions were prepared to contain equivalent amounts of chlorine so that 0.1 N sodium chloride contained one mole per liter while N strontium chloride contained 0.5 mole per liter. For the non-electrolytes such as dextrose or glycerol, N solutions were prepared that contained one mole per liter.

Density determinations were made on 5% gelatin solutions which were prepared in the following manner. The material used was a grade A1 gelatin intended for culture media. In order to obtain gelatin containing a constant amount of moisture regardless of humidity changes in the atmosphere, the stock material was dried for two and one-half hours in an electric oven at 50–60°. It was then broken into small bits by passing it through a food chopper. The ground gelatin was kept in a desiccator. For each sample 5 g. was weighed out and transferred into a dry Erlenmeyer flask; 100 cc. of the desired solvent was then measured into the flask with a buret. Solution of the gelatin was effected by holding the flasks at the temperature of the thermostat, 35.2°, and shaking them frequently. The densities were determined with the aid of the Ostwald modification of the Sprengel pycnometer, one arm of which was equipped with a ground-glass cap while the other arm was fitted with a glass tube having a small bulb and bent in the shape of an elbow. With the pycnometer thus fitted, it was entirely submerged in the constant temperature bath, only the tip

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[8] Loeb, "Proteins and Theory of Colloidal Behavior," McGraw-Hill Book Co., New York, **1922**, pp. 195–231.

of the elbow tube extending above the surface of the water. The hydrogen-ion concentrations of the acids were determined by the hydrogen-electrode method using a potentiometer sensitive to 0.2 or 0.3 millivolt.

Method of Calculation

The volume of the pycnometer was determined in the usual way. The density difference, d, was arrived at quite directly: the difference in weight between the pycnometer plus the gelatin sol and the pycnometer plus the pure solvent was divided by the volume of the pycnometer. A concrete example taken from the results will make the statement clearer. For 5% gelatin solution in N hydrochloric acid we find,

$$\begin{array}{lll} N\ \text{HCl solution} + \text{pyc.} & = & 50.8212\ \text{g.} \\ N\ \text{HCl} \qquad\qquad\ + \text{pyc.} & = & \underline{50.4740} \\ \qquad \text{Diff.} & = & \ \ 0.3472 \end{array} \qquad \frac{0.3472}{\text{vol. of pyc. } (27.17565)} = d = 0.012776$$

An attempt was made to standardize the various steps in the determinations as much as possible. For instance, the time required to weigh out the gelatin was always about the same.

Data and Discussion of Results

Density-difference determinations were made using both electrolytes and non-electrolytes. The former group consisted of acids (acetic, nitric, hydrochloric, sulfuric, and phosphoric) and salts (chlorides of the alkali and alkaline earth metals); the latter group was composed of organic substances such as urea, glycerol, and alcohol. Table I gives the values of d for 5% gelatin in acids of various concentrations as shown.

Table I

The Effect of Acids on the Density Difference

5% gelatin at 35.2°

Concn. N	Acetic	Nitric	Hydrochloric	Sulfuric	Phosphoric
2	0.01395	.....[a]	0.01237	0.01145	0.01304
1	.01440	0.01243	.01277	.01251	.01369
0.1	.01470	.01361	.01356	.01377	.01441
0.001	.01470	.01425	.01448	.01435	.01465

[a] 2 N Nitric acid coagulated the gelatin; therefore, no determination of the density could be made.

It will be seen that in all cases d increases as the normality becomes less, or as the solution becomes more nearly pure water. The value of d is 0.01443 when only distilled water is used. Apparently all values of d approach that for water, although the values for N, 0.1 N, and 0.001 N acetic exceed it.

The hydrogen-ion concentrations of the acids were determined with the hydrogen electrode and are tabulated in Table II as Sörensen values.

TABLE II

THE SÖRENSEN VALUES OF THE ACID SOLUTIONS

Concn. *N*	Acetic *P*H	Hydrochloric *P*H	Sulfuric *P*H	Phosphoric *P*H
2	1.86	0.03	0.48	1.00
1	2.17	0.45	0.51	1.23
0.1	2.71	0.90	1.07	1.60
0.001	3.55	2.10	2.51	2.67

In Fig. 1 are plotted the values of *d* on the y-axis against the *P*H values of the acids on the x-axis. The value of *d* for pure water is 0.01443 and is plotted at *P*H 5.4. The first observation is that the density increases with *P*H and comes to a maximum; the Sörensen value for this maximum is very near to 3.0. From the maximum at *P*H 3.0, the density curves drop toward a minimum, probably near the iso-electric point. The curves for the variation of density with hydrogen-ion concentration would, therefore, in a measure be identical with those given by Loeb[9] for the variation of total swelling, osmotic pressure, conductivity, and viscosity. The hydration of gelatin increases with the Sörensen value up to or near *P*H 3.0 as measured by the density of gelatin sols in various concentrations of acids.

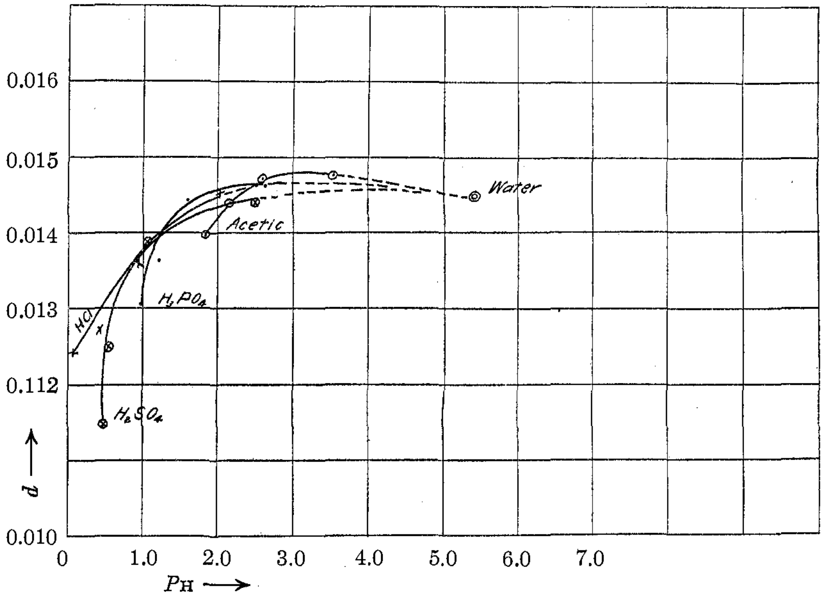

Fig. 1.—Effect of acids on *d*. The strength of the acids is expressed in Sörensen values

If the density increase is due to the formation of a shell of highly compressed water around the gelatin particle, we should expect the density

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[9] Loeb, "Theory of Colloidal Behavior," McGraw-Hill Book Co., New York, 1922, p. 38.

to vary with the amount of acid in solution, since there is a contest set up between the gelatin particles and the acid for the possession of the water.[10] In Fig. 2 the values of *d* are plotted against the normality of the acids. When this is done, the acids fall (roughly) in the order of their strengths, the acetic and phosphoric coming above hydrochloric, nitric, and sulfuric. The hydration of the gelatin is not as much affected by acetic acid as by sulfuric, for instance. From their positions on the graph, we may arrange these five acids in a series as regards their effect on the hydration of gelatin: acetic<phosphoric<hydrochloric<sulfuric and nitric.

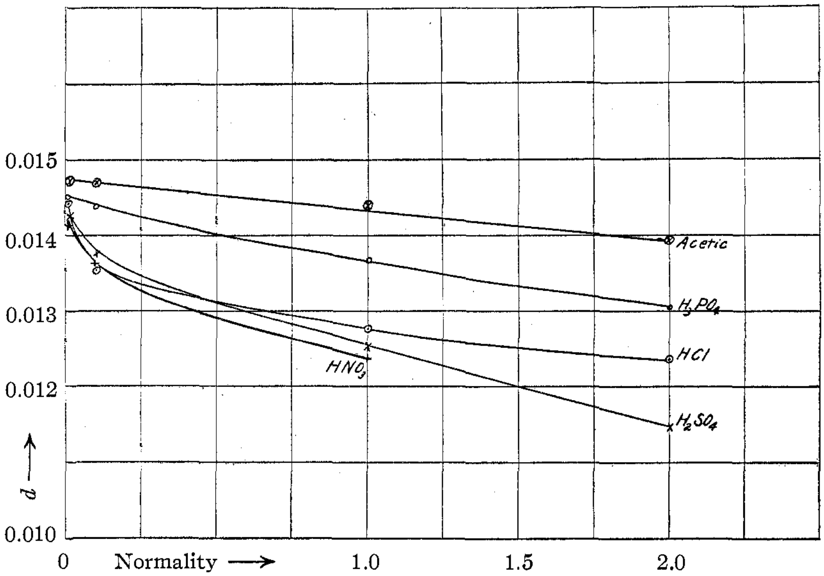

Fig. 2.—The effect of acids on *d*. The strength of the acid is expressed in normality

In Table III are given the effects of salts on the density difference.

TABLE III

THE EFFECT OF SALTS ON THE DENSITY DIFFERENCE

5% gelatin at 35.2°

Concn. *N*	LiCl	KCl	NaCl	$CaCl_2$	$SrCl_2$
2	0.01201	0.01037	0.01051	0.01004	0.00825
1	.01303	.01222	.01179	.01310	.01063
0.1	.01416	.01363	.01340	.01356	.01321
0.001	.01402	.01376	.01358	....	.01364

The values of *d* are of the same order as those obtained for the acids. On plotting *d* against the normality (with reference to the chlorine atom), in the same manner as for the acids, we get the curves of Fig. 3. The

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[10] Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. h., Leipzig, **1922**, pp. 920–978.

value of *d* for gelatin in water for this series of runs is 0.01365 and is not plotted on the graph to avoid confusion. As the solutions become more dilute, the values of *d* approach that for pure water in all cases except lithium. It acts anomalously in that *d* for 0.1 *N* and 0.001 *N* solutions exceeds *d* for water. In the cases of these salts we again have evidence of the hydration being affected by a contest between the gelatin and the salt for the possession of the water. An interesting point to note is that the curves for the chlorides of the alkali metals fall above those for the alkaline earth metals and in the order of their absorption on charcoal.[11] These cations can be arranged in a series with respect to their effect upon the density: Sr>Ca>Na,K>Li.

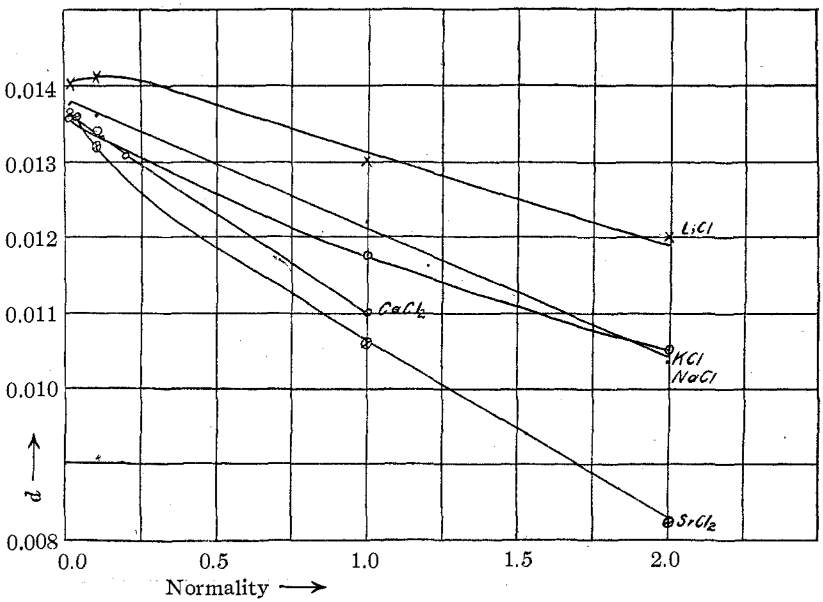

Fig. 3.—Effect of salts on *d*

Similar density determinations were made on gelatin solutions with various concentrations of non-electrolytes, all organic substances including

TABLE IV

THE EFFECT OF NON-ELECTROLYTES ON THE DENSITY DIFFERENCE

5% gelatin at 35.2°

Concn. *N*	Dextrose	Urea	Glycerol	Methyl alc.	Ethyl alc.
2	0.01201	0.01312	0.01357	0.01485	0.01514
1	.01326	.01357	.01388	.01457	.01489
0.1	.01414	.01428	.01444	.01439	.01458
0.001	.01440	.01424	.01462	.01431	.01421

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[11] Odén and Andersson, *J. Phys. Chem.*, **25**, 311 (1921). Osaka, *Mem. Coll. Sci. Kyoto*, 1, No. 6 (1915).

dextrose, urea, glycerol, methyl and ethyl alcohol. The results are given in Table IV, and shown graphically in Fig. 4. In general, the organic substances have much less effect on the hydration than do the acids and salts. A curious effect is obtained with the two alcohols: apparently their presence encourages the hydration of gelatin, since the density difference, *d*, increases with the increase in concentration of the alcohol. The slope of the curves is opposite in sign to those of the acids and salts.

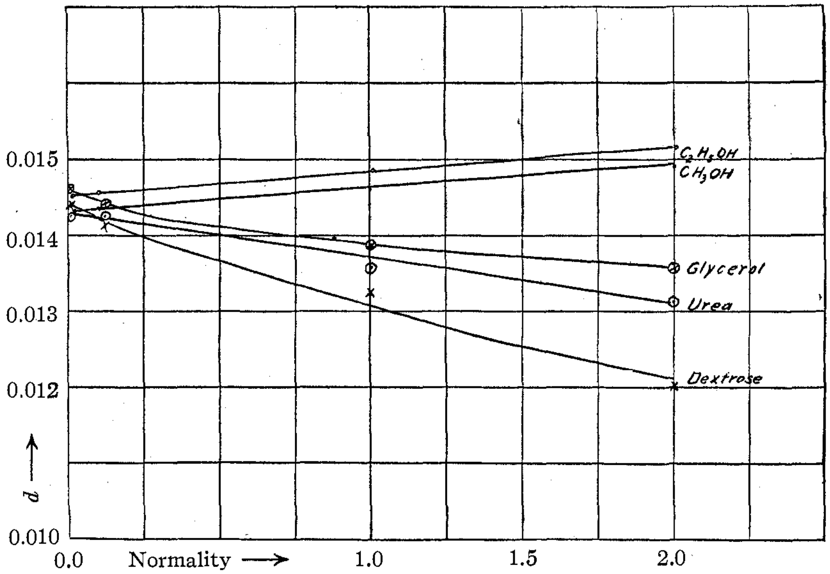

Fig. 4.—Effect of some organic substances

It is interesting to note in connection with the effect of salts and nonelectrolytes on the density of the gelatin that Pauli and Handovsky[12] found that the viscosity of acid egg albumin was increasingly depressed by increased additions of salts such as sodium sulfate, sodium nitrate, sodium phosphate, and uranium nitrate. These same authors[13] find that neutral salts depress the viscosity of alkaline egg albumin and that the salts of the alkaline earth metals are more effective than the salts of the alkali metals. Handovsky[14] also finds that such organic substances as urea, caffeine, glycocoll, and aminobenzoic acid depress the viscosity of protein sols.

Summary

1. The variation in density of gelatin sols in different concentrations of acids was determined. It was found that for all the acids used, the den-

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[12] Pauli and Handovsky, *Biochem. Z.*, **18,** 340 (1909).

[13] Pauli and Handovsky, *ibid.*, **24,** 239 (1910).

[14] Handovsky, *ibid.*, **25,** 518 (1910).

sity increases with an increase in hydrogen-ion concentration up to a maximum value at about *P*H 5.0, after which the density curves drop toward a minimum (probably coming at *P*H 4.7, although more data are necessary before a definite statement may be made).

2. The curves for the variation of viscosity of proteins with change in Sörensen values also have a maximum at *P*H 3.0–3.2 dropping to a minimum at the iso-electric point, *P*H 4.7, as shown by Loeb and Pauli. The similarity of the density curves to the viscosity curves adds further verification to Pauli's theory of hydration of proteins.

3. The acids may be arranged in a series as to their effect on hydration: acetic<phosphoric<hydrochloric<sulfuric<and<nitric.

4. It was shown that the effect of alkali and alkaline earth chlorides on hydration is of the same order as for acids and that the cations may be arranged in a series in the order of their effectiveness: Sr>Ca>Na,K>Li.

5. Non-electrolytes did not affect the hydration to nearly as great an extent as did the acids and salts. The anomalous action of methyl and ethyl alcohols seemed to indicate that they favored the hydration.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE DETERMINATION OF TITANIUM BY REDUCTION WITH ZINC AND TITRATION WITH PERMANGANATE[1]

BY G. E. F. LUNDELL AND H. B. KNOWLES

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Introduction

Most texts leave the impression that the reduction of titanium by zinc in acid solution, as in a Jones reductor,[2] is a slow and difficult process. As a matter of fact, titanium is no more difficult so to reduce than iron[3] and the reduction proceeds quickly and quantitatively to the trivalent stage.

The treatment of the reduced titanium solution is also usually made a matter of special precautions, such as catching the liquid in a measured excess of a standard permanganate solution or in an atmosphere of hydrogen or of carbon dioxide. Here, precautions are well taken, as trivalent titanium is very easily oxidized. The question, therefore, concerns the choosing of the most effective preventive and is answered by the use of

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[1] Published by permission of the Director of the Bureau of Standards of the United States Department of Commerce.

[2] For details concerning the construction of a Jones reductor, consult such texts as Treadwell-Hall, "Analytical Chemistry," Vol. II, 5th Ed., J. Wiley and Sons, p. 638, or Scott, "Standard Methods of Chemical Analysis," Vol. I, 3rd Ed., p. 320.

[3] W. F. Hillebrand in *U. S. Geol. Survey, Bull.*, **700**, p. 169, calls attention to this fact and to a communication from Mr. J. A. Holladay, Chief Chemist of the Electro Metallurgical Co., on the same subject.