erated in small concentrations of electrolytes.

It is shown in this paper that the dyeing characteristics of benzopurpurine 4B and its isomer are explained by the particle size of the colors in the dye-bath and by the sensitivity of the dyes to the building up of agglomerates in the presence of electrolytes. Other factors in the dyeing process are related to these two. Thus the distribution of the dye between the bath and the fiber obviously depends on the salt sensitivity of the dye while the particle size of the micelles is the controlling factor in establishing the rate at which dyeing proceeds.

Summary

Benzopurpurine 4B is shown to be much more highly aggregated in solution than its isomer by additions of sodium chloride or sodium sulfate. The degree of aggregation of benzopurpurine 4B is readily influenced by the electrolyte concentration and the temperature. The particle size of the micelles and the salt sensitivity (sensitivity to agglomeration at low concentrations of electrolytes) of the dyes are shown to be controlling factors in their dyeing characteristics.

WILMINGTON, DEL. RECEIVED OCTOBER 11, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

Contractions Accompanying the Swelling of Gelatin[1]

BY LEO FRIEDMAN AND BETTY BROWN

Two distinct methods are used to study the volume changes which take place when a solid protein is placed in a solution. The first measures the volume change of the solid alone, which is commonly known as swelling, whereas the second measures the total volume change. The results of the first method indicate the degree of water absorption, while those of the second supposedly indicate the degree of hydration. A knowledge of the latter should lead to a better understanding of the phenomenon of swelling.

Relatively few measurements of the total volume changes occurring during the swelling of proteins have been made, and the results which have been published are not in good agreement. Marie and Marinesco[2] have reported that the total volume contractions observed when gelatin is placed in solutions of varying *p*H is a minimum at the isoelectric point and increases in acid and basic solutions. The range covered by their experiments was *p*H 3.5 to 8.5, at both of which points they reported maxima. Neville, Thies and K'Burg[3] and Svedberg[4] have reported the opposite effect, namely, that when contraction is plotted against *p*H a maximum contraction is observed at the isoelectric point while increasing or decreasing *p*H is accompanied by a decrease in the contraction.

Experimental Procedure.—The total volume changes were measured by use of a simple dilatometer similar to that described by Hampton.[5] An air-dry gelatin disk (containing 15% water) was placed in a small copper gauze container and suspended in carbon tetrachloride by means of No. 35 copper wire threaded through the capillary. After the system had come to an equilibrium in the thermostat at 10°, the gelatin was raised into the aqueous solution by means of the wire. Eastman Kodak electrodialyzed gelatin was used in all of the experiments. Solutions of acid and base were made up from standard solutions of hydrochloric acid and sodium hydroxide, and the *p*H was determined electrometrically before and after swelling.

Experimental Results.—The contraction per gram of the original gelatin occurring when the disks were permitted to swell in water at 10° for varying intervals of time is shown in Fig. 1. Since the curve becomes nearly horizontal after about eight hours, the determinations in acid and basic solutions were made after this time interval. The contraction per gram of water imbibed, also shown in Fig. 1, was found to be a constant quantity.

The effect of *p*H upon the total volume contraction during the swelling of gelatin at 10° is shown

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[1] Presented at the 88th meeting of the American Chemical Society, Cleveland, Ohio, September, 1934.

[2] C. Marie and N. Marinesco, *Compt. rend.*, **193**, 736 (1931).

[3] H. A. Neville, E. R. Thies and R. B. K'Burg, *Ind. Eng. Chem.*, **22**, 57 (1930).

[4] The Svedberg, THIS JOURNAL, **46**, 2673 (1924).

[5] H. C. Hampton, *Science*, **63**, 49 (1926).

in Fig. 2, where the contraction in cu. mm. per gram of dry gelatin is plotted against the *p*H of the solution after eight hours of swelling. It is to be observed that the contraction is a minimum in the isoelectric region and rises to a maximum on each side at *p*H values in good agreement with those reported by Marie and Marinesco.[2] In more acid solutions a second minimum was found at *p*H 2.2, while in more basic solutions the contraction became steadily smaller and reached a value of zero at *p*H 13. A comparison of Fig. 2 with a swelling curve shows that the maxima of contraction fall at *p*H's nearer the isoelectric point than do the swelling maxima.

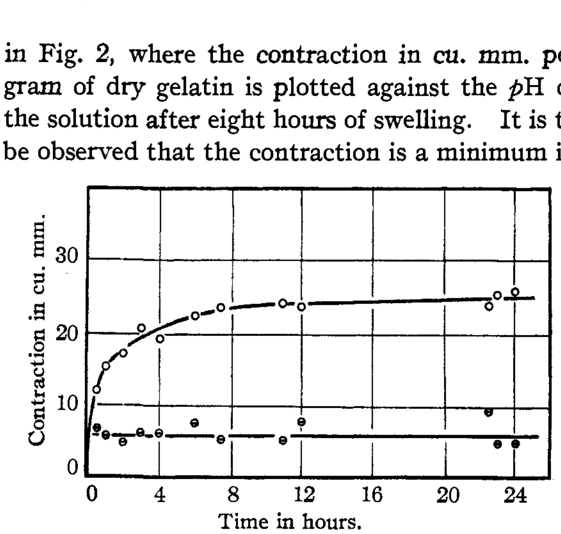

Fig. 1.—Total volume contraction in gelatin–water systems: ○, contraction per gram of dry gelatin; ⊖, contraction per gram of water imbibed.

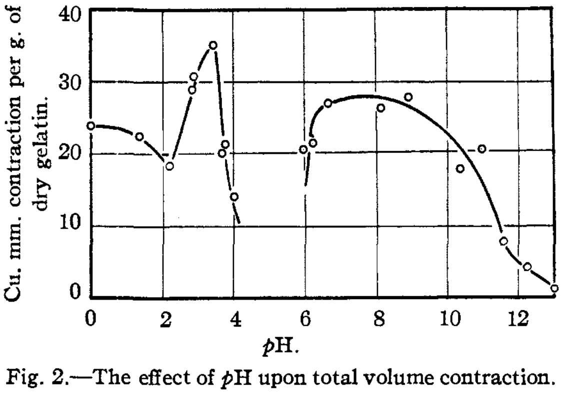

Fig. 2.—The effect of *p*H upon total volume contraction.

Discussion.—The hydration of hydrophilic colloids has been ascribed to the formation of a compressed water sheath about the colloidal micelle, which increase in density is to be expected from the fact that every liquid shows a heat of wetting with every solid which it wets. Regardless of whether the water is held about the micelle by gravitational[6] or electrostatic forces,[7] there will be a resulting increase in the density of the water in the immediate neighborhood of the micelle. Accepting this viewpoint, the more highly hydrated a system becomes during swelling, the greater will be the volume contraction.

Neville, Thies and K'Burg[3] reported that maximum hydration occurred at the isoelectric point and decreased with the addition of either acid or base. This was based upon results such as shown in Fig. 3, which was taken from their work. We wish to call attention to the curve in Fig. 4 which was obtained by using values from our own data corresponding to the *p*H values indicated by Neville, Thies and K'Burg. Had these authors extended their work into the *p*H range nearer the isoelectric point, they would have found the total volume contraction to be a minimum at the isoelectric point instead of a maximum.

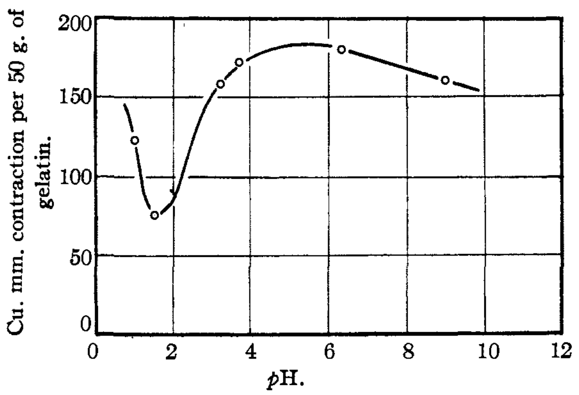

Fig. 3.—The effect of *p*H upon total volume contraction.

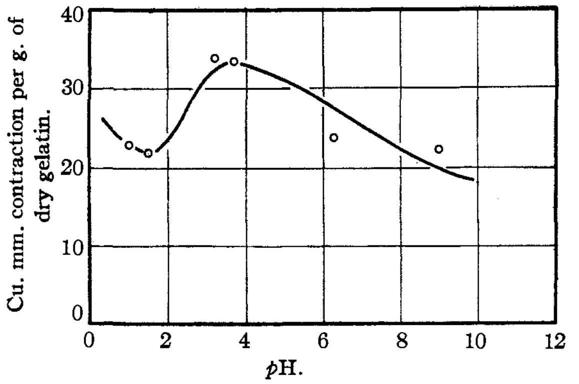

Fig. 4.—The effect of *p*H upon total volume contraction.

That the total volume contraction should increase as one leaves the isoelectric region is to be expected. Viscosity data indicate a higher degree of hydration, and as the colloidal micelles become more highly charged the water mantle will be sub-

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[6] H. G. Bennett, *J. Am. Leather Chem. Assoc.*, **13**, 270 (1918).

[7] H. Pallmann, *Vierteljahrschr. Naturforsch. Ges. Zürich*, **76**, 16 (1931).

jected to an increasing electrical pressure capable of compressing the water. It seems, however, that in experiments such as described in this work, a factor not previously considered should be brought in.

When 85% dry gelatin is permitted to swell at 10°, it is still in the gel condition after eight hours of swelling. It has been demonstrated that a gelatin gel contains many tiny pores filled with liquid.[8] For a 15% gel these openings would have an average radius of about 1 mμ and this value would be correspondingly smaller in more concentrated gels. When water is dispersed into very small droplets, the internal pressure increases according to the formula $P = 2\sigma/r$, in which σ is the surface tension and r is the radius of the spherical drop. In a drop of water 1 mμ in radius, the internal pressure would be about 1440 atmospheres, which pressure is sufficient to cause a 5% compression. In a drop one-tenth this size, the internal pressure would be ten times as great and the resultant compression could be as high as 20% of the original volume.

It is true that when water is dispersed in a gelatin gel it is not dispersed in the form of spherical droplets, nor do we know anything about the interfacial tension between the dispersed water and the solid gelatin walls. Furthermore, nobody knows to what extent the above formula is valid for drops of 1 mμ radius. The above figures can, however, serve as a first approximation demonstrating the possibility that some of the contraction in total volume when protein systems swell may be due to increased internal pressure when the liquid is highly dispersed.

That this factor is actually effective in the experiments herein described is indicated by the fact that the maxima in volume contraction fall nearer the isoelectric point than do the swelling maxima. At the swelling maxima the contraction due to dispersion of the water is at a minimum although the hydration and the electrostatic pressure on the water are probably at maxima at this point.

Summary

Measurements have been made to determine the influence of *p*H on the total volume contractions accompanying the swelling of gelatin at 10°.

A definite minimum in contraction was found at the isoelectric point, maxima at *p*H's 3.5 and 8, and a second minimum at *p*H 2.2.

Contraction in total volume has been attributed (1) to hydration, (2) to increased electrical field around the colloidal micelle as the isoelectric region is left and (3) to compression resulting from dispersion of water in the gel and the resultant increase of internal pressure.

CORVALLIS, OREGON RECEIVED OCTOBER 19, 1934

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[8] L. Friedman and E. O. Kraemer, THIS JOURNAL, 52, 1295 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Ethers in Liquid Ammonia

BY THOMAS H. VAUGHN, R. R. VOGT AND J. A. NIEUWLAND

White, Morrison and Anderson[1] prepared diethyl ether, ethyl *n*-butyl ether and several aromatic ethers by the Williamson method in liquid ammonia at approximately −33° and atmospheric pressure. They obtained ethyl *n*-butyl ether in 19% yield but stated that di-*n*-butyl ether could not be made by this method, presumably due to the insolubility of sodium *n*-butylate in liquid ammonia, and they did not attempt the synthesis of other dialkyl ethers. The present work shows that at higher temperatures and pressures the dialkyl ethers may be readily prepared in liquid ammonia, and that, due to the presence of water or alcohol as impurities, dialkyl ethers frequently occur as by-products in the practical preparation of alkylacetylenes from sodium acetylide and alkyl halides in liquid ammonia.

In most of our experiments a solution of two moles of sodium in 2 liters of liquid ammonia was prepared in the pot of a standard 10-liter aluminum pressure cooker. A high speed Monel metal down-beating propeller stirrer was mounted just beneath the surface of the solution, and 2 mols of an alcohol was run in. A vigorous reaction took place but the foaming could be easily controlled by raising or lowering the stirrer blade. In thirty to forty-five minutes when the formation of the alcoholate was complete, 2 mols of alkyl

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[1] White, Morrison and Anderson, THIS JOURNAL, 46, 961 (1924).