conditions (1)

$$\frac{c}{c_0} = \frac{1}{\sqrt{4\pi D_0 t}} \int_{\infty}^{h} e^{-\frac{h^2}{4D_0 t}} \, dh \qquad (2)$$

This is identical in form with the equation for the probability integral

$$Z = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{\infty}^{h} e^{-\frac{h^2}{2\sigma^2}} \, dh \qquad (3)$$

where z varies from zero to 1. From equations 2 and 3 it is evident that

$$\sigma^2 = 2D_0 t \text{ or } D_0 = \frac{\sigma^2}{2t} \qquad (4)$$

Values of z as a function of h are readily available in tables and it is also possible to purchase probability graph paper[13] ruled from 0 to 100% in such a way that a plot of z *vs.* h is a straight line. The value of σ is equal to the difference in the h intercepts at 50% and either 15.87 or 84.13%. D_0 can of course be estimated from the 15.87 or the 84.13% intercept alone but it has been found safer to plot the values of c *vs.* h on probability paper and draw the best straight line through the points to obtain the h intercepts. To do this the c values are converted to C' values from 50 to 100 by the relation

$$C' = (50c/c_0) + 50 \qquad (5)$$

or the equivalent reaction for values from 0 to 50

$$C' = 50 - (50c/c) \qquad (6)$$

Figure 4 shows data from two photographs of one run with 1 N potassium chloride. The D values obtained, 1.8 and 1.9 $\times 10^{-5}$, show satisfactory agreement with the integral value of 1.85 $\times 10^{-5}$, calculated from the data given by Vinograd and McBain[14] corrected according to Gordon.[15] This

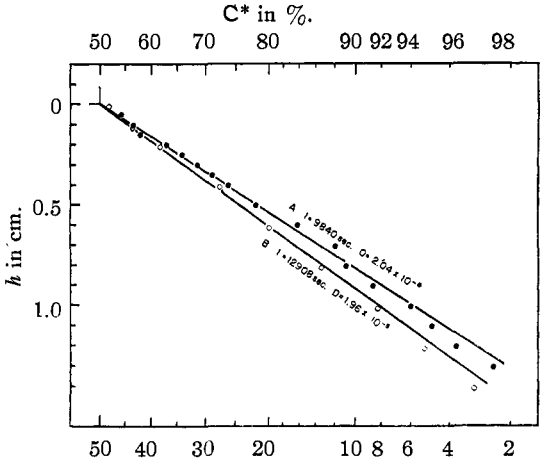

Fig. 4.—Diffusion of 1 N KCl at 25° plotted on probability paper.

agreement is partially fortuitous since D for potassium chloride varies by 10% over the range from 0 to 1 N. The probability integral method is essentially equivalent to the height and area method for analysing curves of dc/dh obtained by the scale method.[16]

Summary

1. An apparatus is described in which diffusion takes place in a narrow chamber along one face of a prism into an effectively infinite volume of solvent.

2. The initial boundary is formed by flooding the top of the thin chamber.

3. The concentration of diffusing material is determined from the angle of total reflection which is recorded photographically.

4. The apparatus is suitable for solutions containing of the order of 1% solute.

(13) From Keuffel and Esser.

(14) J. R. Vinograd and J. W. McBain, THIS JOURNAL, **63**, 2008 (1941).

(15) A. R. Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).

(16) E. M. Bevilacqua, *et al.*, *ibid.*, **46**, 309 (1945).

EUGENE, OREGON RECEIVED MAY 7, 1949

[CONTRIBUTION FROM THE STANFORD RESEARCH INSTITUTE, STANFORD UNIVERSITY]

Studies of Protein Foams Obtained by Bubbling[1]

BY WILLIAM C. THUMAN,[2] A. G. BROWN[2] AND J. W. MCBAIN

Introduction

The foaming of protein solutions is of theoretical interest, and also has wide applications in the baking industry and in fire fighting practice. It is known to be greatly dependent upon *p*H and the presence of salts, though but little systematic work has been published in this field.

Recently it was shown by Perri and Hazel[3] that a soybean protein solution exhibited a maximum foaming capacity in the neighborhood of the isoelectric point. Barmore[4] in studying the properties of egg white foams as a problem of the baking industry reported that organic acids and acid salts considerably increase foam stability. Peter and Bell[5] found the stability of foams from the protein of whey to be increased by addition of

(1) (a) This investigation was conducted under Contract N-7onr 321 between The Stanford Research Institute and the Office of Naval Research, supervised by Professor J. W. McBain; (b) presented at the 115th meeting of the American Chemical Society, San Francisco March, 1948.

(2) Present address: Stanford Research Institute, Stanford, California.

(3) J. M. Perri and F. Hazel, *J. Phys. Colloid Chem.*, **51**, 661 (1947).

(4) M. A. Barmore, Colorado Agricultural College Technical Bulletin, 9, 1934.

(5) P. N. Peter and R. W. Bell, *Ind. Eng. Chem.*, **22**, 1124 (1930).

alkali, sodium sulfite, or a mixture of calcium chloride with calcium hydroxide. In the results of Clark[6] with hydrolyzates of blood protein the maximum foam volume was obtained from a solution near the isoelectric point.

Most of the work on the foaming capacity of protein solutions has been carried out with protein materials of uncertain composition or consisting of obvious mixtures. Thus, it seemed desirable to extend the work of Perri and Hazel employing other pure proteins. For the present study purified egg albumin and salmine sulfate were selected. With the egg albumin, previous work could be greatly extended. Salmine sulfate was chosen because its isoelectric point is at a *p*H of 12, in sharp contrast to both α-soybean protein and egg albumin with isoelectric points respectively 4.1 and 4.6 to 4.8.

Preliminary experiments were carried out by Irving M. Abrams,[7] who found that single bubbles on salmine sulfate solutions show a sharp maximum in lifetime at about *p*H 10. We have found that the foaming capacity of 0.5% salmine solutions is a maximum around this same *p*H and that solutions of egg albumin also show a maximum in foaming capacity slightly on the acid side of the isoelectric point.

The effects of *p*H and of added electrolytes have been examined in some detail for the purified egg albumin.

Materials.—The two proteins used in these experiments were a protamine sulfate (salmine sulfate) supplied by Eli Lilly and Company and a sample of hen egg albumin from the laboratories of the Harvard Medical School. As we received it, the latter sample had been recrystallized three times and dialyzed against water and dried. Freshly prepared solutions of protein were used each day. The concentrations in these experiments were 0.05% for the albumin and 0.5% for the protamine. This concentration of egg albumin approximates in nitrogen value the soybean solution used by Perri and Hazel.[8] The higher concentration of the protamine was necessary due to its poor foaming characteristics.

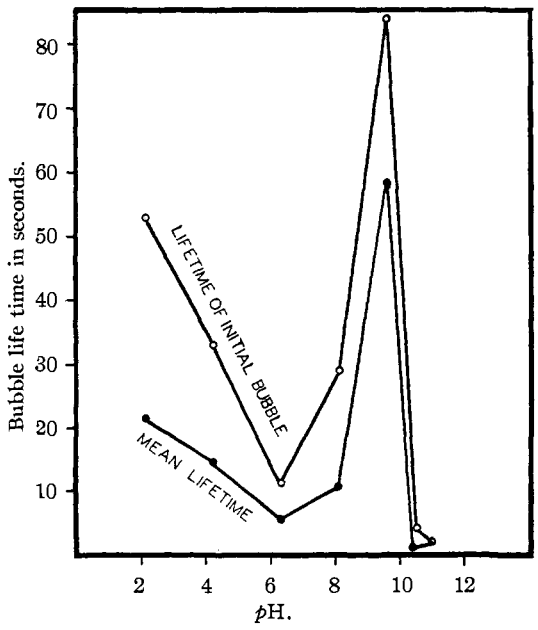

Fig. 1.—Effect of *p*H on lifetime of single bubbles on 0.5% salmine sulfate.

Method.—For determinations of foaming capacity, 1.0 cc. of liquid was transferred to the porous plate of a modified Stiepel type foam meter[8] by means of a Blodgett pipet. During foam formation the rate of air flow through the porous plate was maintained at 16 cc. per minute until there was no further increase in the volume of the foam. This maximum volume was recorded. While individual values for foaming capacity are probably subject to an error, in the extreme, of 2 cc., most curves were obtained as the result of several independent determinations in order to minimize errors in foam volume and also errors in *p*H caused by fouling of the glass electrode by the protein.

Except where otherwise indicated, the protein was dispersed in distilled water and made up to volume with the required solution of electrolyte. For some experiments, clear solutions of the protein were obtained by dissolving the protein in a minimum volume of 10^{-3} *M* hydroxide and making it to volume with sufficient solution of electrolyte to give the required electrolyte concentration.

When a range of *p*H values was desired, the first *p*H of a solution to be tested was that of the solution as prepared. Subsequent determinations on the acid side of this first value were made after stepwise additions of hydrochloric acid; on the alkaline side by additions of potassium hydroxide. Determination of *p*H was made with a Model G Beckman glass electrode *p*H meter employing standard or blue glass electrodes in the appropriate ranges.

In those experiments requiring conditions free from carbon dioxide, boiled distilled water was used in preparation of the solutions. Access of carbon dioxide to the solution during the experiment was prevented by a current of air free from carbon dioxide flowing into and out of the container in which the solution was enclosed. Air flow, adjustment of *p*H, and removal of the sample by means of the Blodgett pipet was made possible by an opening in the top of the container. In those experiments requiring saturated solution of carbon dioxide, the solution was enclosed in the above container, and carbon dioxide from dry ice was allowed to flow into and out of the vessel during the experiment.

Experiments on Life of Single Bubbles by I. M. Abrams.—Preliminary experiments were carried out on the life-time of single bubbles released from an orifice and floating to the surface of 0.5% protamine solutions at different *p*H values. These experiments were carried out in closed vessels to exclude dust and minimize evaporation.

The effect of *p*H on bubble lifetime as indicated by the lifetime of initial bubbles at different *p*H values and by the average lifetime at these values is shown in Fig. 1 for 0.5% protamine solutions. While the variation of bubble life at any observed *p*H was very great, a sharp maximum in stability was observed somewhat on the acid side of the isoelectric point. Stability was at a minimum at about *p*H 6 and increased again at low *p*H values.

Foams with Salmine Sulfate.—The results with single bubbles suggested the desirability of extending the investigation to actual foams, both of the protamine and of albumin. The results for the foaming capacity of 0.5% protamine solutions at different *p*H values are shown in Fig. 2. At the concentration used (0.5%) the foams obtained were weak and poorly characterized. However, a broad maximum in foaming capacity does appear somewhat on the acid side of the isoelectric point.

(6) N. O. Clark, "A Study of Mechanically Produced Foam for Conbatting Petrol Fires," His Majesty's Stationery Office, London, 1947.

(7) Present address: Chemical Process Co., Redwood City, California.

(8) S. Ross, *Ind. Eng. Chem., Anal. Ed.*, **15**, 329 (1943).

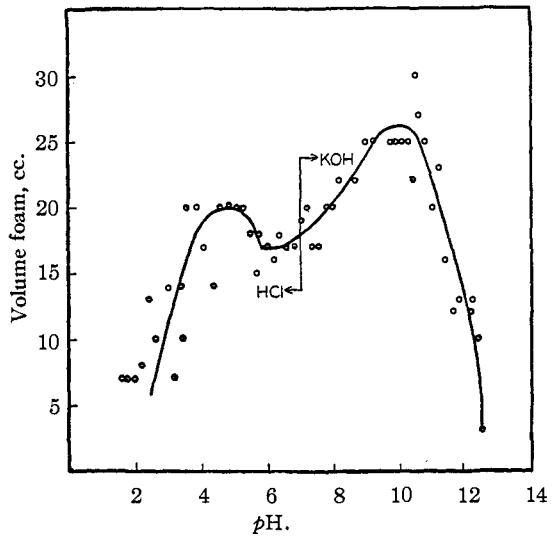

Fig. 2.—Effect of *p*H on foaming capacity of 1.0 cc. of 0.05% protamine sulfate.

Foams with Egg Albumin

Standard Foaming Capacity Curve.—Well-defined foams were obtained using a 0.05% aqueous solution of albumin at different *p*H values, especially in the region of maximum foaming capacity. Greatest foaming occurs on the acid side (*p*H 3.7 to 4.0) of the normal isoelectric point of albumin (*p*H 4.6 to 4.8), and at very high and very low *p*H values, as shown in Fig. 3. The absence of foam between *p*H's 6 and 11 is very striking. Figure 3 will appear dotted for reference in all later figures.

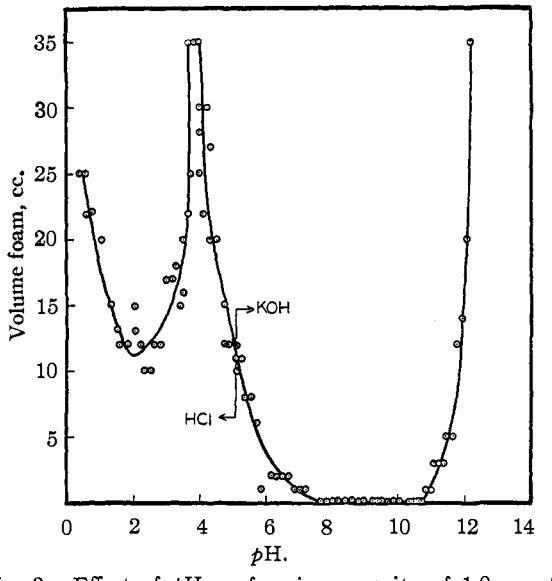

Fig. 3.—Effect of *p*H on foaming capacity of 1.0 cc. of 0.05% egg albumin.

These solutions were exposed to air and therefore contained carbon dioxide. However, determinations of foaming capacity in the *absence* of carbon dioxide give values which, within experimental error, appear to fall on the same standard curve. Saturating the solutions with carbon dioxide slightly decreases the amount of foam produced near the isoelectric point. These results are shown in Fig. 3a.

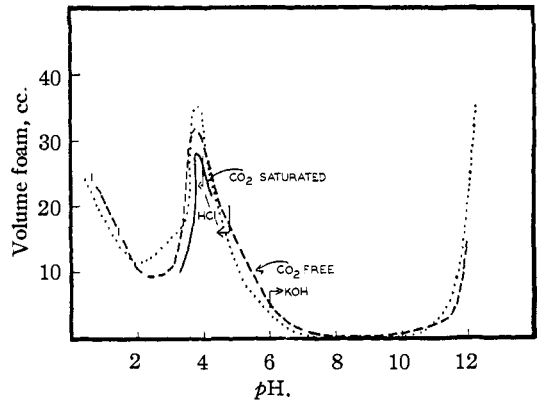

Fig. 3a.—Effect of *p*H on foaming capacity of 1.0 cc. of 0.05% egg albumin in absence of carbon dioxide. Effect of saturating the solution with carbon dioxide.

Effect of Added Weak Acids at Various *p*H's Adjusted with Potassium Hydroxide or Hydrochloric Acid.—The effect of anions on the maximum foaming capacity was investigated in the region of the isoleectric point by foaming 1.0 cc. of 0.05% albumin in 10^{-3} *M* salt solutions, adding hydrochloric acid or potassium hydroxide as required. Arrows on the accompanying figures indicate initial *p*H values. It is to be noted that the characteristics of albumin in the region of the isoelectric point are of interest to the baking industries. The effects of adding acetic acid, potassium acid tartrate, citric acid and phosphoric acid are shown in Figs. 4 and 5. The curve for a saturated solution of carbon dioxide has been mentioned previously (Fig. 3a).

Effect of Added Salts.—The effect of cation valence at different salt molarities is shown in Table I. The results

TABLE I

EFFECT OF CATIONS ON FOAM CAPACITY OF 0.05% EGG ALBUMIN

Molarity of added salt	KCl		$CaCl_2$		$Ca(NO_3)_2$		$Th(NO_3)_4$	
	*p*H	Foam, cc.	*p*H	Foam, cc.	*p*H	Foam, cc.	*p*H	Foam, cc.
0	5.09	10	5.09	10	5.2	12	5.2	12
10^{-1}	5.45	12	5.85	12	5.0	14	2.3	25
10^{-2}	5.1	14	6.0	12	4.9	14	2.9	50
10^{-3}	5.2	12	5.8	10	4.9	11	3.3	45
10^{-4}	5.1	12	5.0	10	4.8	12	4.0	6
10^{-5}							4.2	6
10^{-6}							5.0	17
10^{-7}							5.2	14

were not at all similar to those which might have been expected from the work of Perri and Hazel, and it became obvious that salt effects should be investigated over a range of *p*H values for each concentration of salt. Such studies are shown in Fig. 6 for 10^{-2}, 10^{-3} and 10^{-4} *M* potassium chloride and for 10^{-3} *M* calcium chloride. The curve for the calcium chloride–potassium hydroxide system (Fig. 6) was obtained later and will be discussed in connection with Fig. 9.

Effect of Degree or Kind of Dispersion of the Albumin.—Albumin "solutions" as ordinarily made up, and as used in all the above experiments, were obtained by simply dissolving the albumin in distilled water. These solutions had a *p*H of 5.05 to 5.1 and were slightly turbid. *Clear* solutions were obtained by dissolving the protein in 10^{-3} *M* potassium hydroxide. Foaming capacities of such solutions were determined over a range of *p*H values obtained by additions of hydrochloric acid or further potassium hydroxide and are shown in Fig. 7. Access of carbon dioxide

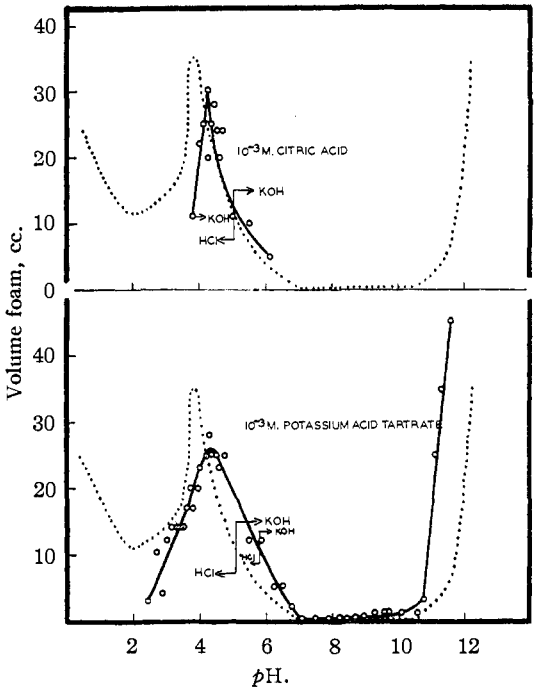

Fig. 4.—Effect of 10^{-3} M potassium acid tartrate or 10^{-3} M citric acid on foaming capacity of 1.0 cc. of 0.05% egg albumin at different pH values.

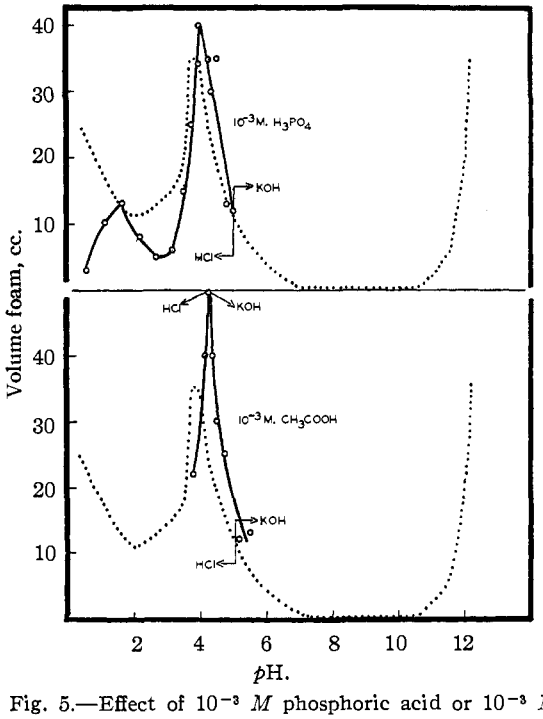

Fig. 5.—Effect of 10^{-3} M phosphoric acid or 10^{-3} M acetic acid on foaming capacity of 1.0 cc. of 0.05% egg albumin at different pH values.

to these solutions was prevented. For comparison, results are shown also in Fig. 7 for the foaming capacity of a *clear* solution of albumin dissolved in 5×10^{-4} M potassium carbonate, to which hydrochloric acid or potassium hydroxide was then added to adjust the pH.

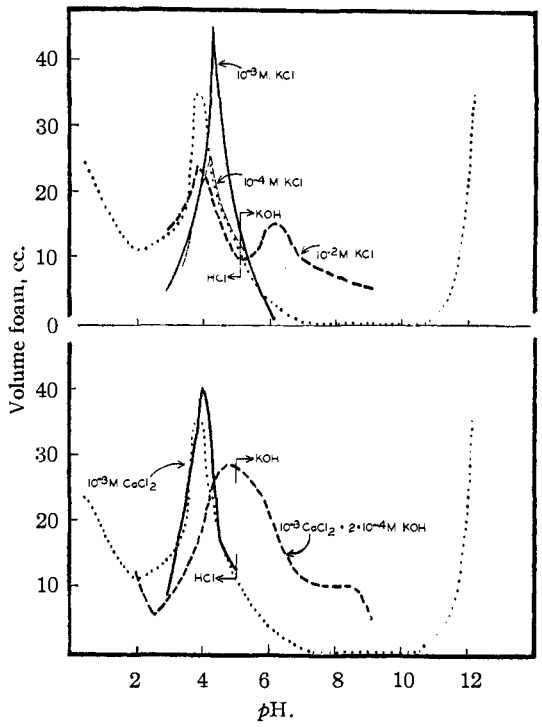

Fig. 6.—Effect of various concentrations of potassium chloride on foaming capacity of 1.0 cc. of 0.05% egg albumin at different pH values. Effect of 10^{-3} M calcium chloride on the foaming capacity of 1.0 cc. of 0.05% albumin solution at various pH values; comparison of the foaming of egg albumin originally dispersed in 10^{-3} M calcium chloride solution at pH 5.95 with the foaming of egg albumin originally *dissolved* in 10^{-3} M potassium hydroxide and then made 2×10^{-4} M in potassium hydroxide and 10^{-3} M in calcium chloride.

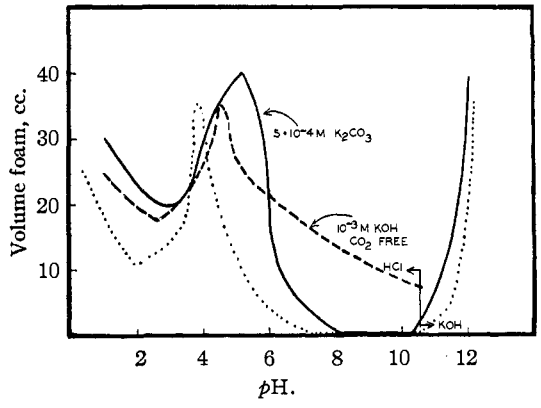

Fig. 7.—Foaming capacity of 1.0 cc. of 0.05% egg albumin showing effect of *dissolving* the albumin in 10^{-3} M potassium hydroxide or in 5×10^{-4} M potassium carbonate, access of carbon dioxide from the air prevented at all times.

It is apparent that much more foam is produced in the alkaline region when the protein is first dissolved in alkali.

The lesser foaming in potassium carbonate solution as compared to potassium hydroxide solution may be due to a depressing effect of carbonate or bicarbonate ion or it may be due to an effect of the slightly lower initial *p*H of the potassium carbonate solution.

Experiments with Dissolved Egg Albumin in Presence of Barium Ion.—After showing the importance of first *dissolving* the egg albumin in 10^{-3} *M* potassium hydroxide, a series of experiments was carried out with egg albumin *dissolved* in a minimum volume of 10^{-3} *M* barium hydroxide (50 mg. albumin in 20 cc.) and then adjusted to various concentrations of barium ion by adding water or concentrated barium hydroxide, making the albumin 0.05%. Access of carbon dioxide was prevented. Adjustment of *p*H was made with hydrochloric acid. The five curves are presented in Fig. 8. The very great increase in foaming caused by the barium ion in the alkaline range is strikingly evident. Near *p*H 4, on the contrary, foaming decreases regularly with increasing concentrations of barium salt.

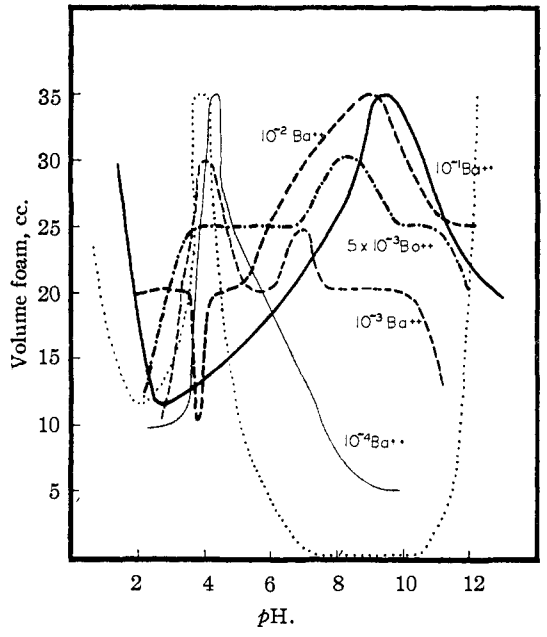

Fig. 8.—Foaming of 0.05% egg albumin *dissolved* originally in barium hydroxide and kept carbonate free, with *p*H adjusted by adding hydrochloric acid, showing decrease in foaming at *p*H 4 caused by barium salt and great increase at *p*H's 7 to 10.

Dispersed and Dissolved Egg Albumin in Presence of Barium Chloride.—Figure 9 shows the results of further experiments in which on the one hand, 0.05% egg albumin was initially *dispersed* in 10^{-3} *M* barium chloride at *p*H 5.4, and *p*H's adjusted with potassium hydroxide or hydrochloric acid; and, on the other, initially *dissolved* in a minimum of 10^{-3} *M* potassium hydroxide, then adjusted to 2×10^{-4} *M* potassium hydroxide and 10^{-3} *M* barium chloride, with further adjustments of *p*H by adding hydrochloric acid. The initial point of each series is indicated by a cross on the curve in Fig. 9. A similar effect for calcium chloride is shown in Fig. 6. It is seen that the degree or kind of dispersion of the protein and the presence of alkaline earth ion are both important in promoting foaming in the alkaline range.

Effect of Sea Water.—Ability of a material to foam in sea water is of importance in certain special foam applications. In this connection the egg albumin, dissolved at a concentration of 0.05 % in synthetic sea water (*p*H 8.2), gave 15 cc. of foam by the bubbling method; whereas, after adjusting the *p*H by small additions of hydrochloric acid or potassium hydroxide, the following foam volumes were obtained: *p*H 7.2, 17 cc.; *p*H 9.0, 32 cc.; *p*H 10.0, 20 cc. In distilled water at these *p*H values the foaming capacity of the pure albumin is negligible (Fig. 3). It is interesting that the sea water causes a maximum in foaming in about the same *p*H region as does barium ion at a concentration equivalent to the total alkaline earth concentration of the sea water (Fig. 8).

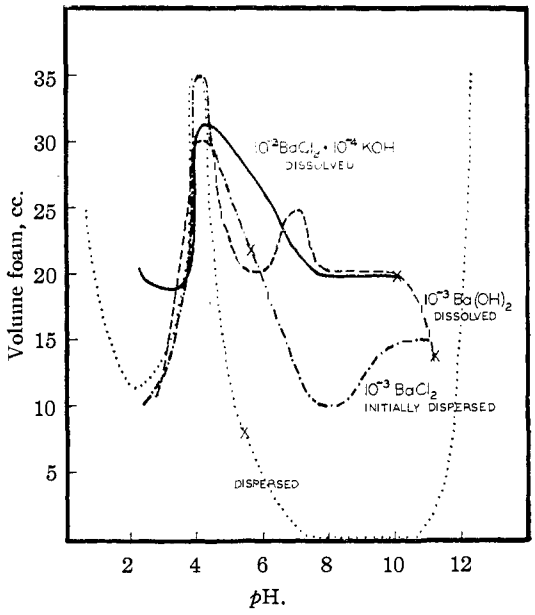

Fig. 9.—Results in presence of 10^{-3} *M* barium ion, in absence of carbon dioxide. Comparison of effect of barium ion on egg albumin initially *dispersed* at *p*H 5.4 (marked by cross) with effect of egg albumin initially *dissolved* at *p*H 10.1 (marked by cross) and with the effect of barium ion on egg albumin originally dissolved at *p*H 11.2 (marked by cross) in 10^{-3} *M* barium hydroxide. The dashed line as in Fig. 8 represents solutions made in barium hydroxide with *p*H's adjusted by adding hydrochloric acid; the full line, solutions made in 10^{-3} *M* potassium hydroxide diluted to 2×10^{-4} *M* potassium hydroxide and kept 10^{-3} *M* barium chloride with *p*H's adjusted by hydrochloric acid; the heavy dot-dash line refers to a dispersion containing 10^{-3} *M* barium chloride with *p*H's adjusted by potassium hydroxide or hydrochloric acid.

Discussion

It is seen that the foaming properties of proteins are complex and necessitate isolating the various factors by obtaining series of experiments over the whole *p*H range while studying one factor at a time. This is illustrated by the different curves in our figures.

The first point noticed is the pronounced maximum in the foaming of the albumin and protamine solutions at a *p*H slightly on the acid side of the isoelectric point. The albumin solutions also showed high foaming capacity at very high and very low *p*H values. The foaming capacity at this maximum appears to be the same whether the albumin was originally dispersed at *p*H 5 or originally dissolved at *p*H 10 (in 10^{-3} *M* potassium

hydroxide or 10^{-4} *M* barium hydroxide) although the position of the maximum is slightly shifted.

In the alkaline ranges albumin originally *dissolved* in potassium or barium hydroxide froths freely; whereas, if the albumin is first merely dispersed in water at *p*H 5–5.4 and the *p*H increased by adding potassium hydroxide, the albumin does not froth at all between *p*H's 7 and 11.

If sufficient barium ion is added to albumin dissolved in 10^{-3} *M* hydroxide, the frothing at *p*H 9 equals the maximum normally observed near the isoelectric point, but additional barium salt did not improve the foaming further. However, at *p*H 4, barium salt has the opposite effect, and lessens the foaming, as is seen in Fig. 8. Barium is seen to be much more effective than calcium or potassium in promoting foaming in the alkaline range. With increasing amounts of barium ion, maximum foaming occurs at increasingly higher *p*H values.

There appears to be a significant correlation between denaturation and maximum foaming. When foaming was a maximum, either at *p*H 4 for the "standard" curve or at *p*H 9 through the influence of barium ion, a residue which could not be redissolved was observed after collapse of the foam; when foaming was weak, no such denatured residue was found. Adam[9] has discussed denaturation in connection with protein films obtained either by spreading the protein on the surface of water or by adsorption of the protein at the air–protein solution interface, and has associated the effect with the "unfoldment" of the protein molecule in the surface film. It would appear from our results that only under conditions of optimum foaming is the protein adsorbed at the air–solution interface in the form of a fully extended coherent film.

Some further insight as to the nature of the adsorbed albumin film in the foam may be gained from the fact that, under conditions of optimum foaming, the air–liquid surface area produced was estimated by bubble size measurements to be of the order of magnitude of one square meter for each 5 mg. of albumin present in the original solution (surface tension 62 dynes/cm.). Comparisons with the results of Hughes[10] for the spreading of albumin at the air–water interface suggest that, under conditions of maximum foaming, the adsorbed surface film is of the "gel" type.

It therefore appears that the essential condition for maximum foaming is that the protein solution be capable of yielding readily a fully extended, semi-rigid, coherent protein film adsorbed at the air–solution interface. It would seem to be suggested that this condition is fulfilled when there is a minimum net charge on the protein complex—at very high and very low *p*H values due to suppression of ionization of the protein, at the isoelectric point due to "self-neutralization," and at intermediate values due to neutralization of free COO^- or NH_3^+ groups by cations or anions, respectively. Our results actually depart from this idealized concept in two respects. Maximum foaming actually appeared on the acid side of the isoelectric point and anion effects were not apparent. It is possible that the isoelectric point of albumin in an "unfolded" or extended condition at the air–water interface may be slightly different from that of the protein in solution although the possibility of a shift due to the presence of electrolytes is not completely eliminated. The reason the expected anion effect did not appear in our results may be that in this *p*H range (below *p*H4 for albumin) the weak acids involved were almost completely undissociated.

It is interesting to note that Gorter and coworkers[9] have found that the rate of spreading of proteins at the air–water interface is a maximum at the isoelectric point and at very high and very low *p*H values. They showed that in the alkaline range cations improve spreading according to a typical lyotropic series and also that anions had similar effects on the acid side of the isoelectric point.

Zhukov and Bushmakin[11] observed a maximum stability of benzene emulsions stabilized with gelatin at the iso-electric point, *i. e.*, where the surface tension and viscosity are at a minimum. Two minimum stability points were observed at *p*H 2.5 and 9.5 coinciding with maximum viscosities. They concluded that non-hydrated and undissociated gelatin molecules serve best for emulsification.

Our results appear to amplify and extend those of Perri and Hazel[3] and offer possible explanations for those of others. Thus Barmore observed a maximum foaming capacity of fresh whole egg white at *p*H 8, which may be due to inorganic cations, although globulins are of course also present. In so far as whey proteins may be compared with egg albumin, the results of Peter and Bell[5] correlate satisfactorily with ours.

It appears from this work that in any study of the foaming properties of proteins it is important to be aware of electrolytes, either added or originally present in the protein, to consider the degree or kind of dispersion of the protein and to observe the foaming characteristics over a wide range of *p*H values for each concentration of electrolyte used.

Summary

1. Proteins produce maximum foam somewhat on the acid side of the isoelectric point. This is shown by single bubbles and by frothing for egg albumin (*p*H 4) and protamine (*p*H 10).

2. This maximum is enhanced by dissolving the egg albumin in 10^{-3} *M* acetic acid.

3. If egg albumin is merely dispersed to a somewhat turbid "solution" at *p*H 5, it does not foam in the range *p*H 7 to 11.

(9) N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., 1941, pp. 87–92.

(10) A. H. Hughes, *Trans. Faraday Soc.*, **29**, 214 (1933).

(11) I. I. Zhukov and I. N. Bushmakin, *J. Russ. Phys.-Chem. Soc.*, **59**, 1061 (1927).

4. If first dissolved in 10^{-3} *M* alkali (potassium hydroxide or barium hydroxide) it foams freely in the alkaline range.

5. Alkaline earth ion or salt greatly promotes foaming in the alkaline range, but may minimize it on the acid side.

6. The data presented, considered in the light of previous knowledge, indicate that different proteins follow a general pattern in their foaming behavior and that this pattern is similar to that exhibited by other properties of proteins.

STANFORD, CALIFORNIA RECEIVED JANUARY 17, 1949

[CONTRIBUTION NO. 1240 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Preparation and Properties of Vanadium Nitrosyl Chlorides

BY ARTHUR GREENVILLE WHITTAKER[1] AND DON M. YOST

In connection with an investigation of vanadium tetrachloride, VCl_4, it was observed that a beautiful, dark purple, coarsely crystalline substance forms readily when dry nitric oxide is passed through a solution of vanadium tetrachloride in carbon tetrachloride. Similar crystalline materials result when dry nitric oxide reacts with pure vanadium tetrachloride in either the liquid or vapor state. Although compounds containing the NO group have been previously studied,[2] the reaction products herein described do not appear to have been mentioned in the literature and are therefore new.

Experimental

The vanadium tetrachloride was prepared as described in a previous paper.[3] Nitric oxide was prepared by slowly adding 50% sulfuric acid to a solution which was four formal in potassium nitrite and one formal in potassium iodide.[4] The gas was purified and dried by passing it through successive tubes containing potassium hydroxide, calcium chloride and magnesium perchlorate.

In preparing these new compounds, three different sets of conditions were tried, yielding three different sets of principal reaction products. In all cases a number of products were formed, but the principal ones were the dark purple crystals and vanadium trichloride. Small amounts of nitrosyl chloride and vanadium oxytrichloride were always produced, however. The three sets of reaction conditions and principal products are: (1) Nitric oxide reacting with vanadium tetrachloride in the vapor phase gave the solid $V_2Cl_3(NO)_5$, and a large fraction of vanadium trichloride; (2) Nitric oxide passed into liquid vanadium tetrachloride resulted in the precipitation of the compound V_2Cl_7NO; (3) The insoluble solid VCl_4NO was formed when nitric oxide was passed into a dilute (say 10%) carbon tetrachloride solution.

All reactions were started at room temperature, but as considerable heat is evolved the exact temperatures during reaction cannot be specified. No attempt was made to estimate the heat of reaction. The compounds were purified by subliming them from one end of a pyrex tube (50 cm. × 2.5 cm.), which was filled with dry air or carbon dioxide at one atmosphere, to the other. Although sublimation begins at about 45°, the hot end of the tube was maintained at 135° and the cold end at room temperature. The residue at the hot end of the tube was always vanadium trichloride. Before the crystals were removed from the tube the collection end was placed in a furnace at 50° overnight to distill any liquid away from the crystals

Densities were determined pycnometrically; carbon tetrachloride served as the liquid. Magnetic susceptibility measurements were made by the Gouy method.

Extensive analyses of the various preparations were made using the following methods. (1) Vanadium was determined, in sulfuric acid solution, with standardized permanganate. (2) Chlorine was precipitated as silver chloride and weighed. (3) Nitrogen was determined by first oxidizing to nitrate with alkaline permanganate the nitric oxide or nitrous acid formed when the purple crystals react with water. The excess permanganate was reduced with hydrogen peroxide and the manganese dioxide filtered off. Nitrogen in the filtrate was determined by the Kjeldahl method, using aluminum metal in sodium carbonate solution as a reducing agent.

Results and Properties of the Compounds.—The average values of the results of the analyses and of the measurements of the densities and magnetic susceptibilites are presented in Table I. As indicated there the results of the analyses were best satisfied by compounds with the empirical formulas VCl_4NO, V_2Cl_7NO and $V_2Cl_3(NO)_5$.

All the compounds gave off a colorless gas and ultimately yielded a blue solution when placed in water. The blue solution was due to vanadyl ion, VO^{++}, and the gas was identified as nitric oxide. The amount of nitric oxide liberated by each compound is indicated in Table I. In the case of V_2Cl_7NO the rate of solution was slower and it was possible to observe a brown solution in the immediate vicinity of the crystals as they reacted with water. The brown color was much like that due to VO^+ which one gets on dissolving vanadium trichloride in water.

Long, dark purple, opaque crystals were formed by each of the compounds. Microscopic examination revealed that dark purple light was transmitted by small crystals. Also, the crystals were birefringent, and they show parallel extinction. The crystals of VCl_4NO and $V_2Cl_3(NO)_5$ were needle-like, and had a tendency to form penetration twins. The crystals of V_2Cl_7NO were shorter prisms that tended to form hemispherical tufts of the prisms like pins in a pin cushion.

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