Physical-Chemical Properties of Whey Protein Foams

Stanley H. Richert

Functionality of proteins in foams theoretically depends upon their abilities to reduce interfacial tension, to increase liquid phase viscosity, and to form strong films. These abilities are facilitated by alteration of tertiary and quaternary protein structures, which are dependent upon physical-chemical conditions. Foam density and stability are simultaneously affected; however, they correlate poorly. Several studies have been conducted to optimize low-fat whey protein foams. Optimum conditions have been observed for solids (or protein) concentration, pH, heat treatment, ionic strength, and Al^{3+} concentration. Performance has been improved by addition of Ca^{2+}, H_2O_2, and hexametaphosphate in isolated studies. It has been impaired by addition of sucrose, lipids, and surfactants and by reduction of oxidation-reduction potential. Interaction effects have been evident for several combinations of variables. Reversible improvement of foaming by heat treatment has been observed in several studies and appears to be related to protein-lipid interaction. Heat setting of low-fat whey protein foams has been disappointing. Little work has been reported on the physical-chemical behavior of whey proteins in high-fat foams.

During the past decade, several processes have been developed to commercial scale to prepare whey protein products with minimal denaturation. The premise of these developments was that the proteins would be valuable for their functional properties, such as foaming, emulsifying, acid solubility, heat coaguability, etc.

Egg albumen is the food protein system most recognized and utilized for its foaming ability and has been the target in most of the whey protein foaming studies. Under typical household whipping, it will form a foam eight-ten times the volume of liquid in less than 5 min that is stable for about 30 min. Most importantly, the foam will withstand incorporation of additional solids and will set to a rigid, more permanent structure by heating. Whey proteins can accomplish the first three feats; however, they have been disappointing in the latter two.

In this paper, I (1) review theoretical concepts of foams as related to proteins, (2) discuss physical-chemical variables affecting whey protein foams, (3) describe the reversible improvement of whey protein foams by heat treatment, and (4) suggest that foaming properties of whey proteins should be studied under the physical-chemical conditions present in the intended application.

THEORETICAL ASPECTS

Foams may be classified according to the number of phases present. The simplest form would be pure gas bubbles enveloped within a continuous phase of pure liquid. This form would be stable only at very high liquid viscosities or if gravitational forces were very small. In food systems, foams are often very complex, including several phases such as a mixture of gases, subdivided solids, subdivided liquids, and multicomponent solutions of water, polymers, and surfactants. Prediction of their behavior is exceedingly difficult. Typical food foams are either quite high in fat or oil content or very low. Compositions between the two extremes are difficult to whip and the foams collapse quickly. Little work has been published on the behavior of whey proteins in high-fat foams; therefore this review will be concerned primarily with low-fat foams.

Most foams are sufficiently high in gas content so that the liquid phase exists as lamellae between adjacent bubbles. The surface area of the lamellae becomes very large (hundreds of square meters per kilogram of liquid) (Bikerman, 1965). The surface energy at a surface tension of 0.045 N/m would be 4.5 N-m/kg, roughly equivalent to a 0.002 °C rise in temperature. This energy is added in the form of work to form the foam. The two most common methods of forming experimental foams are whipping with mixers or beaters and bubbling the gas phase into the liquid phase through small orifices such as sintered glass. In whipping, bubbles are formed by cutting the surface, whereby atmospheric gas is incorporated into the liquid. A coarse foam is formed initially and is made more disperse by continued cutting of bubbles. Bubbling methods form bubbles which rise through the liquid. Once formed, bubbles are not likely to become smaller; however, they may become larger. This method can easily incorporate different gases. Cooney (1974) found that N_2 was superior to O_2, H_2, and CO_2 for whey protein foams. He related gas solubility and diffusivity to foam stability.

The time required to form the optimum foam under given conditions varies according to the physical and chemical situation. Speed of whipping is important to food process economy and consumer acceptance; therefore it may be considered a dependent variable. For experimental comparisons, however, it is essential to evaluate a foaming liquid under optimum conditions. One way to achieve this economically is to foam to a recognized end point, such as when the foam takes on a semi-solid character as indicated by the formation of stable peaks (Richert et al., 1974).

FOAM STABILITY

Instability of foams is indicated by drainage of liquid and by an increase in the size of bubbles. Cooney (1974) demonstrated that the rate of drainage from a given foam is proportional to the amount of remaining liquid, i.e., first order. He expressed stability as half-life. However, a lag is evident because considerable time elapses in more stable foams before any drainage occurs. In fact, the time elapsed before the first drop of liquid separates is an excellent measure of foam stability (Richert et al., 1974).

Liquid may separate from a foam either by drainage from the lamellae or by rupture of bubbles (Shaw, 1970). Drainage from the lamellae can be compared to flow of liquid between parallel plates; however, due to the very small thicknesses, surface viscosity and capillary forces become very important. Orientation of surface active solutes, including proteins, will establish gradients in composition and therefore in viscosity. Film thickness, viscosity, and surface properties are important determinants of the rate of drainage. Quantitative treatment of

Ralston Purina Company, St. Louis, Missouri 63188.

0021-8561/79/1427-0665$01.00/0

Table I. Effect of Solids and Protein Content upon Whey Protein Foams

solids content, %	protein content, %	overrun, %	stability, min	study
5	2.5	700	0.16 (1st drop)	McDonough et al. (1974)
15	7.5	600	0.50	
25	12.5	400	8	
35	17.5	0	0	
	2	1140[a]	65 (half-life)	Kuehler and Stine (1974)
	3	1270	83	
	4	1300	94	
	5	1370	102	
	6	1450	110	
5.5	3.4	610	6 (half-life)	Cooney (1974)
10	3.5	610	9	
11	6.8	610	9	
17	10.4	610	12.5	
20	7	610	15	
30	10.5	610	18	
2.5	1.5	290[a]	poor	Hansen and Black (1972)
3	1.8	350	poor	
4	2.4	410	good	
5	3.0	540	good (dry)	

[a] Estimated from specific volume, % overrun = (SV − 1) × 100%.

foam theory is too lengthy to present here and is available elsewhere (Cooney, 1974; Shaw, 1970; Bikerman, 1965).

Rupture of lamellae may result from thinning of films due to random disturbances. Stretching and thinning is opposed by a local increase in surface tension (Gibbs effect). The surface tension gradient results in a flow of surface active molecules to the area to regain equilibrium, resulting in increased film thickness (Shaw, 1970). Since this transport takes time (Marangoni effect), the diffusity of solutes and viscosity of the liquid are important. The combined effects, resulting in surface elasticity (Gibbs–Marangoni effect) would be expected to be strongly influenced by protein content, molecular weight, conformation, and any quaternary structure formation. The presence of any additional solid or liquid phases would complicate the situation considerably.

Diffusion of gas from small to large bubbles, due to higher pressure in small bubbles, will also result in instability, since the lamellae become thicker as bubble sizes increase. Of course, the amount of diffusion would depend upon the distribution of bubble sizes. Foam formation by bubbling would be expected to form more homogeneous foams.

PHYSICAL–CHEMICAL VARIABLES

A preliminary evaluation of functional properties of whey protein concentrates (Morr et al., 1973) found widely varying and generally poor foaming properties. Several independent studies followed which attempted to improve foaming through manipulation of compositional and procedural variables (Hansen and Black, 1972; Richert et al., 1974; Cooney, 1974; DeVilbiss et al., 1974; Kuehler and Stine, 1974; McDonough et al., 1974; Haggett, 1976a). Results of these studies will now be compared and summarized according to variables studied.

SOLIDS (OR PROTEIN) CONTENT

Viscosities of protein solutions typically increase exponentially with concentration. Therefore, it would be expected that higher protein contents in foams would result in greater stability. Results of some experiments in which protein (or solids) content was varied are presented in Table I. An optimum solids content appears likely since at low solids, overrun increased with increasing solids content (Hansen and Black, 1972; Kuehler and Stine, 1974) and at higher solids content it decreased (McDonough et al., 1974). The optimum would appear to be near the 10% solids level used in other studies (Richert et al., 1974; Cooney, 1974). It is interesting that Cooney (1974) found the same volume at all concentrations. Perhaps this is because the bubbling method of foaming did not introduce excess gas in any treatment.

Foam stability generally appeared to increase at higher solids content, as expected, except that McDonough et al. (1974) failed to produce a foam at 35%. Perhaps this was due to a high-lipid content in the liquid at that concentration. DeVilbiss et al. (1974) also reported increasing stability with solids content between 0 and 20%. Whey protein foams had better stability than egg albumen at very low solids content but poorer above 10% total solids.

EFFECT OF PH

The pH of the whey protein preparation has been shown in several studies to influence foaming properties; however, the results are difficult to reconcile. The effect of pH appears to depend upon other aspects of the situation, i.e., interaction effects are important. For example, Haggett (1976a) obtained better foam volume and stability at pH 8.5 than at 6.0 for casein whey protein concentrate. However, with WPC from cheese manufacture, volume was greater at pH 6.0 but stability was better at 8.5. With added sucrose, however, the best stability was at pH 6.0 for both cheese and casein WPC. McDonough et al. (1974) had similar results when comparing cottage and cheddar whey. DeVilbiss et al. (1974) reported a maximum foam stability at pH ~4 with WPC from cottage cheese whey.

Some explanations for the differences in response to pH between whey sources are: (1) differences in salt composition, especially Ca^{2+} and phosphate in acid whey, (2) presence of glycomacropeptide in rennet whey, and (3) higher lactic acid/lactate content in acid whey. No data are available to support any of these explanations.

Cooney (1974) found maxima for foam volumes at pHs 5 and 7–8. Reduction and blocking of disulfide groups prevented the higher pH optimum, indicating the involvement of disulfide interchange. This produced a single optimum at pH 5 which he attributed to maximum interfacial protein adsorption because of minimum molecular charge.

Cooney (1974) and Richert et al. (1974) reported interaction effects with sodium dodecyl sulfate and pH; however, the effects were opposite. Cooney (1974) found $NaDodSO_4$ beneficial at high pH, whereas Richert et al.

(1974) found it more beneficial at low pH. Perhaps higher order interactions are involved here. Cooney (1974) reported higher volume with added $NaDodSO_4$ at both pH 4 and 7, although at pH 7 a minimum was observed at 2×10^{-3} M.

It is difficult to conclude anything about the effect of pH upon foaming of whey proteins, except that it is an important variable and needs to be considered simultaneously with other variables in designing experiments.

IONS AND IONIC STRENGTH

Cooney (1974) found that foam stability decreased linearly with the square root of ionic strength, varied by adding NaCl to exhaustively dialyzed WPC. Maximum overrun occurred at 0.05 M ionic strength. He tested Al^{3+}, Ca^{2+}, Ba^{2+}, Na^+, K^+, Li^+ as chloride salts and citrate^{3+}, tartrate^{2-}, SO_4^{2-}, Cl^-, acetate, I^- as sodium salts, all at pH 4.3. Al^{3+} doubled stability, whereas Ca^{2+} and Ba^{2+} reduced stability. Fe^{3+} also produced a large increase in stability. Increasing ionic strength to 0.2 M with Al^{3+} improved both volume and stability at pH 4.2; however, a maximum in stability was observed at 0.04 M at pH 7.0. Ca^{2+} produced minimum stability at 0.2 M at pH 7. The anions caused little effect; however, at pH 4.3 the organic anions would be only partially ionized.

At 0.06 M phosphorus and pH 4.2, various phosphates slightly improved foam volume and stability; however, at pH 7 tripolyphosphate was slightly detrimental to foaming.

Hansen and Black (1972) found that carboxymethylcellulose WPC adjusted with $Ca(OH)_2$ produced better foams than NaOH-adjusted; however, their system can hardly be regarded as typical of other WPC.

More work is needed to further elucidate the complex relationships between ionic strength and species and pH as they affect foaming of whey proteins.

OXIDATION REDUCTION POTENTIAL

Little work has been done to investigate the effects of oxidation state upon foaming. It would be expected to have an effect if disulfide interchange is involved (Cooney, 1974).

An optimum state is likely to exist because a small amount (0.025–0.1%) of H_2O_2 added to CMC-complex WPC improved foam volume and a large amount (0.2%) caused deterioration (Hansen and Black, 1972). Reducing conditions established by Na_2S addition impaired foaming (Richert et al., 1974).

SUCROSE AND LIPIDS

Addition of sucrose before whipping invariably causes decreased overrun but sometimes causes increased stability (Haggett, 1976a; DeVilbiss et al., 1974; Hansen and Black, 1972). The interaction effect between sucrose and pH has already been discussed.

In some applications it is necessary that the foam be capable of carrying sucrose added after whipping. Whey proteins appear capable of this; however, they differ significantly from egg albumen in heat setting of angel food cakes (DeVilbiss et al., 1974). The whey protein cakes rose quickly to maximum height and then collapsed. This appears to be more related to the heat coagulation properties of whey proteins rather than foaming properties. Whey proteins do not form the elastic gel typical of egg albumen but rather form granular precipitates.

Some indications of the amount of lipid required to impair foaming are given in Table II. Foam depressant effects of lipids are well documented for both triglycerides and phospholipids in egg albumen (Cotterill et al., 1965; Smith, 1959). Heating to 60 °C has been suggested to improve the foaming properties of yolk-contaminated egg albumen. Cooney (1974) showed that at least 7% trihexanoate could be added if the sample was heated prior to foaming. In fact, foam stability was improved, probably due to increased viscosity with the added lipids. Foaming of unheated samples was impaired by very low concentrations of trihexanoate and somewhat higher concentration of higher melting triglycerides.

Table II. Lipid Content Required to Impair Foaming

% lipid	(in liquid)	
0.26-0.46	(milk fat)	DeVilbiss et al. (1974)
1-2	(butter fat)	McDonough et al. (1974)
<0.0001	trihexanoate	Cooney (1974)
>7	trihexanoate (heated)	Cooney (1974)
>0.5	tritetradecanoate	Cooney (1974)

The ability of whey proteins to foam in the presence of relatively high concentrations of lipids, if heated prior to whipping, may be an important functional property in some applications.

PREPARATION OF WPC

The unit operation used to fractionate the whey will not be considered a fundamental variable in itself in this discussion. It will primarily affect composition of the protein product and denaturation, which are more fundamentally related to functional properties. The techniques commonly used to manufacture whey protein could probably all produce similar products, if suitable process conditions were chosen. The technique itself is probably not nearly as important as the conditions selected for carrying out the process. Therefore processes and processing conditions have been deemphasized in this paper.

HEAT TREATMENT

Marked improvement of foaming properties of WPC by heat treatment have been reported in numerous studies beginning with Peter and Bell (1930). Whipping time is reduced, overrun is increased and stability is usually much longer. The procedure has been patented (Feminella and Grindstaff, 1976). A heat treatment that results in mild protein denaturation appears optimal, depending upon other physical-chemical conditions. The improvement is spontaneously reversible (Richert et al., 1974), and was not observed in whey proteins prepared by precipitation (Richert et al., 1974; Hansen and Black, 1972). The opposite effect has also been observed, i.e., refrigerated storage can be detrimental to foaming of WPC (Haggett, 1976b).

The optimum heat treatment appears to be dependent upon pH. A statistically significant interaction effect (Richert et al., 1974) indicated that a mild heat treatment (<70 °C) is preferred at pH 5.0, whereas higher temperatures (>80 °C) is preferred at pH 7.0. Similar effects were observed by Haggett (1976a).

Haggett (1976b) theorized that the improvement by heating may result from dissociation of β-lactoglobulin dimers.

Cooney (1974) found that ultracentrifuged WPC preparations did not improve upon heating, indicating possible lipid–protein associations formed by heating.

Perhaps the reason that the improvement is not observed in precipitated proteins is that the lipids are washed out. They would be retained by other WPC manufacturing procedures.

The ultimate in improving whipping properties by heating was demonstrated by Jelen (1973) when he removed heat coagulable proteins from whey and produced excellent foams from the remaining solution. This solution

foamed better at low pH and relatively high solids concentration.

CONCLUSION

The physical–chemical properties of whey protein preparations appear to have large effects upon their foaming properties. Kinds and amounts of carbohydrates, salts, and lipids affect both foam volume and stability. The effect of pH appears extremely complex and dependent upon several other variables. If the food system permits, pH manipulation may improve foaming. Unless lipid contents are very low, foaming properties are markedly improved by a mild denaturation heat treatment.

Future work needs to be done to elucidate further the complex relationships between the variables affecting foaming. Until this is done, the foaming capacity of whey proteins intended for a food system can only be evaluated in a system which closely simulates it.

Whey proteins clearly possess different foaming properties than egg albumen. Their capacity for foam formation has been adequately demonstrated. The challenges now are to utilize them for their unique properties and to utilize them at their maximum potential.

LITERATURE CITED

Bikerman, J. J., *Ind. Eng. Chem.* **57**, 56 (1965).
Cooney, C. M., "A Study of Foam Formation by Whey Proteins", Ph.D. Thesis, University of Minnesota, 1974.
Cotterill, O. J., Seidman, W. E., Funk, E. M., *Poultry Sci.* **44**, 228 (1965).
DeVilbiss, E. D., Holsinger, V. H., Posati, L. P., Pallansch, M. J., *Food Technol.* **28**(3), 40 (1974).
Feminella, J. V., Grindstaff, D. A., U.S. Patent 3 935 323 (1976).
Haggett, T. O. R., *N.Z. J. Dairy Sci. Technol.* **11**, 244 (1976a).
Haggett, T. O. R., *N.Z. J. Dairy Sci. Technol.* **11**, 275 (1976b).
Hansen, P. M. T., Black, D. H., *J. Food Sci.* **37**, 452 (1972).
Jelen, P., *J. Dairy Sci.* **56**, 1505 (1973).
Kuehler, C. A., Stine, C. M., *J. Food Sci.* **39**, 379 (1974).
McDonough, F. E., Hargrove, R. E., Mattingly, W. A., Posati, L. P., Alford, J. A., *J. Dairy Sci.* **57**, 1438 (1974).
Morr, C. V., Swenson, P. E., Richter, R. L., *J. Food Sci.* **38**, 324 (1973).
Peter, P. N., Bell, R. W., *Ind. Eng. Chem.* **22**, 1124 (1930).
Richert, S. H., Morr, C. V., Cooney, C. M., *J. Food Sci.* **39**, 42 (1974).
Shaw, D. J., "Introduction to Colloid and Surface Chemistry", Butterworth and Co., Ltd., London, 1970, p 213.
Smith, C. F., *Poultry Sci.* **38**, 181 (1959).

Received for review May 23, 1978. Accepted September 22, 1978. Presented at the 174th National Meeting of the American Chemical Society, Division of Agricultural and Food Chemistry, Chicago, IL, Aug 1977.

Use of Whey Proteins for Supplementing Tortilla

Viorica Racotta,* Hector Bourges, Andres Navarrete, and Juan Zuckermann

Although the average Mexican diet represents adequate protein intake, additional proteins, such as those obtained from whey sources, would be highly desirable. A simple technique, applicable to small industries, is proposed, consisting of coagulating by heat at pH 4.5, siphoning off the lactose supernatant, decanting into suspended sacks, and drying in a forced air oven at 40–50 °C. The protein concentrate obtained had 54.7% protein, 25.6% fat, 9.9% moisture, 1.3% ash, and 8.7% nonnitrogenous material. The protein efficiency ratio (PER) was 3.28. Enriched tortilla (65% corn protein + 35% whey protein) had a PER of 2.16 in comparison to 2.11 for casein and was well accepted according to panel tests.

International statistics point out that Mexico has a daily protein availability per capita of some 68 g of total protein, of which 18 g are animal protein (Narayana, 1973). However, Mexico is an unevenly developed country, with deficient communications, so that an average figure does not reflect reality. National statistics (Ramirez et al., 1971) distinguish four main types of nutrition areas: good, medium, bad, and very bad. Whereas the first two types show acceptable figures, the last two areas have daily per capita intakes of 1895–2124 kcal, 50–56 g of total protein, and 8–10 g of animal protein, respectively.

Animal protein production is deficient in Mexico. Cheese production, for example, is only about 77 000 metric tons per year (Anuario Estadistico, 1976). Statistical figures for whey production are not available, but, assuming that 8 kg of whey is produced per kilogram of cheese, we estimate a yearly production of some 600 000 tons of whey. Estimating a yield of about 2 kg of crude protein for each ton of liquid whey, the above figure means some 1200 tons of high-quality protein.

There is little information about the use of whey in Mexico. The big cheese plants dry the whey, but it appears that in rural areas whey is generally fed directly to domestic animals; discharge into rivers also seems to be common.

The object of this work is to utilize whey protein recovered under Mexican conditions for human consumption. The process for protein recovery should fulfill the following criteria: (a) the process must be a very simple one, applicable to small-scale industry and to unskilled labor; (b) the recovered protein should be used for enriching a traditional basic food.

Protein recovery may be performed by a heat coagulation process of sweet whey. This protein could be added to tortilla, which is a staple food in the diet of rural populations in Mexico.

EXPERIMENTAL SECTION

We used as raw material cheddar cheese whey of pH 6.0–6.5 and applied a heat coagulation technique at pH 4.5. The scheme of the process is shown in Figure 1. The pH was adjusted by acidifying approximately one-fourth

Instituto Politecnico Nacional, Escuela Nacional de Ciencias Biologicas, Departamento de Graduados e Investigacion en Alimentos, Apartado Postal 42-186, Mexico 17, D.F., Mexico.

0021-8561/79/1427-0668$01.00/0