Comparison of the Emulsifying Properties of Fish Gelatin and Commercial Milk Proteins

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ABSTRACT: We have compared the flocculation, coalescence, and creaming properties of oil-in-water emulsions prepared with fish gelatin as sole emulsifying agent with those of emulsions prepared with sodium caseinate and whey protein. Two milk protein samples were selected from 9 commercial protein samples screened in a preliminary study. Emulsions of 20 vol% *n*-tetradecane or triglyceride oil were made at pH 6.8 and at different protein/oil ratios. Changes in droplet-size distribution were determined after storage and centrifugation and after treatment with excess surfactant. We have demonstrated the superior emulsifying properties of sodium caseinate, the susceptibility of whey protein emulsions to increasing flocculation on storage, and the coalescence of gelatin emulsions following centrifugation.

Key Words: emulsification, gelatin, caseinate, whey protein isolate, emulsion stability

Introduction

ALTHOUGH THE INGREDIENT GELATINE IS PRIMARILY KNOWN for its thermoreversible gelation behavior, it has many other functional applications in food formulations including water-holding, thickening, colloid stabilization, crystallization control, film formation, whipping, and emulsification (Ward and Courts 1977; Hudson 1994). The versatility of the protein gelatin as a hydrocolloid is particularly valued in products like emulsified powders (Kläui and others 1970) where its surface-active and film-forming characteristics can be successfully exploited during the emulsification process and its stabilization and gelation characteristics during the subsequent drying and encapsulation stages.

The class of food proteins most commonly used for their emulsification properties under neutral pH conditions are the milk proteins (Morr 1982; Mulvihill and Fox 1989; Dickinson 1997). Two milk protein ingredients widely used for emulsification are sodium caseinate and whey protein isolate (WPI). For commercial ingredients that are reasonably pure and have not been abused by thermal (or other) processing, it has been reported (Foley and O'Connell 1990) that sodium caseinate and WPI give similar emulsifying capacity at neutral pH, despite their different adsorbed layer structures (Dickinson 1997; Dalgleish 1999). Nevertheless, there are some important functional differences between the caseins and whey proteins, especially relating to their aggregation properties before and after emulsification.

For certain food emulsion formulations, there is interest in replacing gelatin by milk proteins, and vice versa. While it is already known that gelatin forms rather coarse emulsions (Chesworth and others 1985) due to its lower surface-activity at the oil–water interface than casein or whey protein (Dickinson and others 1985, 1989), there has been limited direct comparison of the stability of oil-in-water emulsions made with gelatin and milk proteins under the same well-controlled conditions.

This paper compares the emulsion-stabilizing properties of a set of commercial casein and whey protein ingredients under neutral pH conditions with the properties of a type of fish gelatin that is currently used industrially as an emulsifying agent in oil-soluble vitamin encapsulation. Fine oil-in-water emulsions of 20% dispersed phase were made under identical homogenization conditions using 2 different oil types—a pure hydrocarbon oil (*n*-tetradecane) and a commercial triglyceride oil (rich in triolein). Observations have been made of the effects of emulsifier origin and concentration on emulsion droplet-size distributions and creaming stability. Changes in average droplet size with storage time, and also following centrifugation and/or surfactant addition, have been used to assess the comparative extents of flocculation and coalescence.

Materials and Methods

THE GELATIN SAMPLE G WAS A COMMERCIAL FISH GELATIN from Norland Products Ltd (Nova Scotia, Canada). This low-viscosity gelatin (about 40 kDa) is of a type used by Hoffmann-La Roche for edible oil emulsification and encapsulation. Unlike most mammalian gelatin samples, it does not form a gel under the standard conditions for determining Bloom strength (Leuenberger 1991).

Of the 6 casein samples, C1, C2, and C3 were obtained from New Zealand Milk Products (Rellingen, Germany); C4 and C5 from Lactoprot (Kaltenkirchen, Germany); and C6 from DMV (Veghel, Netherlands). Of the 3 whey protein samples, W1 was from DMV and W2 and W3 from Davisco (Le Sueur, Minn., U.S.A.). Sample C1 (Alanate 188) was a spray-dried sodium caseinate (moisture 3.6%, fat 1.1%, ash 3.6%, calcium 20 mg/100 g), and sample C2 (Alanate 351) was the equivalent potassium caseinate. Sample C3 (Alaco 7005) was a casein hydrolysate (moisture 4.5%, fat 0.8%, ash 5.6%, degree of hydrolysis 33%). Samples C4 (SHV 13) and C5 (LV) were sodium caseinates (5.4% moisture, 1.5% fat) of ash contents 5.6% and 4.2%, respectively. Sample C6 (EM 7) was a sodium caseinate (moisture 5.0%, fat 0.8%, ash 4.0%). Sample W1 (Esprion 580) was an ultra-filtrated spray-dried whey protein concentrate (moisture 4.5%, lactose 4.0%, fat 7.5%, ash 2.5%). Sample W2 (WPI-LE-001-8-919) was a hydrolyzed whey protein isolate (moisture 4.0%, lactose $<1\%$, fat $< 1\%$, ash 5.5%, degree of hydrolysis 6%). Sample W3 (WPI JE 026-7-420) was a whey protein isolate (moisture 4.7%, lactose $<$ 0.5%, fat 0.6%, ash 1.7%).

The *n*-tetradecane (> 99%) was obtained from Sigma Chemicals (St. Louis, Mo., U.S.A.). The commercial triglyceride oil (Trisun 80) was obtained from Danisco (Brabrand, Denmark); its triglyceride fatty-acid composition was 80% oleic, 9% linoleic, 4% stearic, and 4% palmitic. Aqueous phosphate buffer solutions (pH 6.8, 0.05 M) were prepared using analytical-grade reagents and double-distilled water. Sodium azide (0.1%) was used as antimicrobial agent. The nonionic surfactant Tween 20 (polyoxyethylene sorbitan monolaurate) was used as a dispersing agent.

Emulsion preparation and characterization

Oil-in-water emulsions (20 vol% oil, 80% vol% protein solution) were prepared at 20 ± 2 °C under standard conditions using a laboratory-scale jet homogenizer (Burgaud and others 1990) operating at a nominal pressure of 300 bar. The aqueous phase consisted of a solution of the protein in 0.05 M phosphate buffer (pH 6.8) containing 0.1 % sodium azide (in some cases 0.5 M salt was also added). Emulsion droplet-size distributions were determined by multi-angle static light scattering using a Malvern Mastersizer 2000G (Malvern Instruments, Malvern, U.K.) with assumed values of the particle absorption parameter of 0.007 for *n*-tetradecane and 0.005 for Trisun oil. For the purposes of monitoring stability and comparing between systems, the average droplet size was taken as the quantity $d_{43} = \Sigma_i n_i d_i^4 / \Sigma_i n_i d_i^3$, where n_i is the number of droplets of dia d_i.

Creaming stability was determined by monitoring the extent of visible serum separation in emulsion samples of height 50 mm stored quiescently at 20 °C. Stability with respect to flocculation/coalescence was determined by monitoring changes in average droplet size d_{43} with time in regularly mixed emulsion samples. The destabilization was accelerated by centrifugation of some samples at 2×10^4 *g* for 30 min and then redetermination of the droplet-size distribution after careful redispersion of the separated cream layer. In order to distinguish between flocculation and coalescence, emulsion samples were treated with excess surfactant (2% Tween 20) immediately after emulsification or following quiescent storage or centrifugation.

Results and Discussion

Assessing the extent of flocculation

Good emulsification behavior is generally indicated by a narrow monomodal droplet-size distribution and a small average size. A broad or bimodal droplet-size distribution, as determined by multi-angle static light scattering, may be indicative of the presence of a population of larger droplets caused by inadequate homogenization and/or coalescence following storage or centrifugation. Alternatively, a bimodal distribution may indicate the presence of a population of nonreversibly flocculated droplets formed during or shortly after homogenization. Distinguishing between large individual protein-coated droplets and flocculated protein-bridged droplets can be achieved by treating the emulsion with a low-molecular-weight surfactant. Addition of excess surfactant leads to most of the protein being displaced from the oil–water interface and to the subsequent stabilization of the individual oil droplets by the added surfactant.

Figure 1A shows droplet-size distributions for a high-salt gelatin-stabilized emulsion of relatively low protein/oil ratio. Curve (a) represents the initial distribution function $P(d)$ immediately after emulsification. It is strongly bimodal with a minor peak centered around d equals 0.6 μm and a major peak centered around d equals 6 μm. Curve (b) is the distribution function in the presence of Tween 20. We see that, following the addition of excess surfactant, the original peak centered around d about 6 μm has disappeared and is replaced by a skewed monomodal peak centered around d about 0.6 μm. It can be inferred that the original major peak in curve (a) was not due to larger spherical droplets but rather to aggregates of the 0.6 μm primary droplets held together by bridges of protein emulsifying agent. Dissociation of the flocs occurs on addition of surfactant, and so curve (b) corresponds to the actual size distribution of the primary emulsion droplets.

Figure 1B shows droplet-size distributions for an equivalent low-salt caseinate-stabilized emulsion. The initial bimodal distribution function $P(d)$ has a major peak centered around d about 0.6 μm and a minor peak centered around 4–5 μm. In this case, the addition of Tween 20 leads to no significant change in the form of the distribution function. We may therefore infer that this emulsion sample is essentially unflocculated, and that the second peak in curve (a) is really due to the presence of large oil droplets, formed by recoalescence—during, or shortly after, homogenization—as a result of there being insufficient proteinaceous emulsifier present in relation to the new surface area created. Since replacement of adsorbed protein by adsorbed surfactant under quiescent conditions does not affect the primary oil droplet distribution, curve (b) in Fig. 1B has a very similar shape to curve (a).

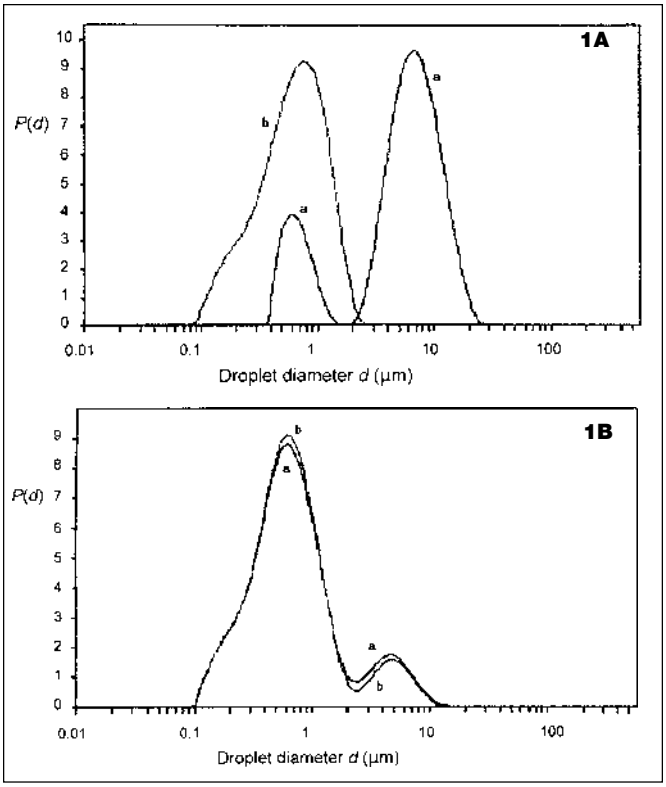

Fig. 1—Examples of (A) a flocculated emulsion and (B) a nonflocculated emulsion. The volume-weighted distribution function *P*(*d*) for droplets of dia *d* is plotted for (A) a gelatin-stabilized emulsion (20 vol% *n*-tetradecane, 0.5 wt% gelatin (sample G), pH 6.8, 0.5 M NaCl, 20 °C) and (B) a casein-stabilized emulsion (20 vol% *n*-tetradecane, 0.5 wt% casein (sample C1), pH 6.8, 20 °C): (a) immediately after emulsification; (b) after emulsification and addition of 2 wt% Tween 20.

Table 1—Comparison of the stability properties of *n*-tetradecane oil-in-water emulsions (20 vol% oil, 1 wt % protein, pH 6.8, 20 °C) made with 10 different protein emulsifiers

Protein emulsifier		Average droplet [a] size d_{43} (μm)		Serum layer [b] thickness (mm)		Flocculation stability [c]	Coalescence stability [d]
sample type	sample code	after 24 h	after 1 wk	after 24 h	after 1 wk		
gelatin	G	1.2	5.5	1	5	×	✓
casein	C1	0.76	0.77	1	2	✓	✓
casein	C2	0.72	0.77	1	2	✓	✓
casein	C3	28	30	32	34	×	×
casein	C4	0.78	0.77	1	2	✓	✓
casein	C5	0.75	0.79	1	2	✓	✓
casein	C6	0.74	0.76	1	2	✓	✓
whey	W1	6.4	8.8	1	13	×	×
whey	W2	13	10	15	19	×	×
whey	W3	1.5	3.9	1	13	×	✓

[a] Estimated experimental error ± 5%
[b] Total sample height = 50 mm; estimated experimental error ± 1 mm
[c] Key: ✓ = no flocculation evident; × = flocculation detected
[d] Key: ✓ = no coalescence evident; × = coalescence detected

Table 2—Comparison of the stability properties of triglyceride oil-in-water emulsions (20 vol% oil, 1 wt % protein, pH 6.8, 20 °C) made with 10 different protein emulsifiers

Protein emulsifier		Average droplet [a] size d_{43} (μm)		Serum layer [b] thickness (mm)		Flocculation stability [c]	Coalescence stability [d]
sample type	sample code	after 24 h	after 1 wk	after 24 h	after 1 wk		
gelatin	G	7.1	21	1	2	×	×
casein	C1	0.74	0.82	1	2	✓	✓
casein	C2	0.84	0.85	1	2	✓	✓
casein	C3	57	71	24	25	×	×
casein	C4	0.87	0.83	1	2	✓	✓
casein	C5	0.82	0.83	1	2	✓	✓
casein	C6	0.83	0.90	1	2	✓	✓
whey	W1	6.9	10	1	2	✓	×
whey	W2	7.4	5.7	10	26	×	×
whey	W3	0.78	0.73	1	2	✓	✓

[a] Estimated experimental error ± 5%
[b] Total sample height = 50 mm; estimated experimental error ± 1 mm
[c] Key: ✓ = no flocculation evident; × = flocculation detected
[d] Key: ✓ = no coalescence evident; × = coalescence detected

The preceding examples refer to 1 emulsion system exhibiting very extensive flocculation (Fig. 1A) and another exhibiting no significant flocculation (Fig. 1B). Sometimes, however, the behavior can lie intermediate between these extremes. That is, there is an initial bimodal distribution, and on addition of excess surfactant, the average size is shifted to smaller *d* values, but the distribution still remains bimodal. In such cases, we may infer that the emulsion prior to Tween 20 addition contains a mixture of some large individual droplets and some flocculated droplets.

Comparison of the 10 protein emulsifiers

A preliminary comparison of the emulsion-stabilizing properties of the 10 protein samples (G, C1-6, W1-3) was carried out with a set of systems containing 1 wt% protein. Table 1 shows the results for *n*-tetradecane as the dispersed phase and Table 2 for triglyceride oil as the dispersed phase.

The gelatin-stabilized emulsions showed considerable growth in average droplet size d_{43} over the storage period. There was evidence for flocculation with both types of oil phase and also some coalescence of triglyceride droplets. Nevertheless, the stability with respect to serum separation appeared moderately satisfactory, in comparison with the whey protein samples (see below).

From the values of d_{43} in Table 1 after 24 h and 1 wk, we can see that all the caseinate samples (C1, C2, C4–6) gave fine *n*-tetradecane-in-water emulsions ($d_{43} < 0.8$ μm) with no significant change in average droplet size over the storage period considered. A similar situation arises also with the caseinate-stabilized triglyceride oil-in-water emulsions (Table 2), although the average droplet sizes were slightly larger ($d_{43} \leq 0.9$ μm). There was no visibly apparent (or inferred) flocculation/coalescence in any of the casein-stabilized emulsions (except with sample C3, see below), and the creaming stability was also excellent (< 5% serum separation after 1 wk).

At the other extreme of behavior, the casein hydrolyzate (sample C3) was found to be a very poor emulsifying agent, leading to highly coarse emulsions, with rapid creaming, and associated extensive evidence of flocculation and coalescence (although no apparent change in stability between 24 h and 1 wk). Also rather poor in terms of the measured stability parameters was the whey protein hydrolysate (sample W2), with either *n*-tetradecane or triglyceride as the oil phase.

The whey protein sample W3 gave fine triglyceride oil-in-water emulsions that were as stable as the caseinate systems. However, the equivalent *n*-tetradecane emulsions were subject to significant flocculation and serum separation after 1 wk of storage. The whey protein sample W1 produced coarser emulsions than sample W3, although the overall stability was roughly similar.

Comparison of 3 protein emulsifier class leaders

Based on the results summarized in Tables 1 and 2, probably the most effective caseinate emulsifier was sample C1—with others, such as C2, quite close behind in terms of performance. The most effective whey protein emulsifier was sample W3. Together with the gelatin sample, the milk protein samples C1 and W3 were selected for more detailed study.

Figure 2 shows the effect of protein emulsifier concentration on the droplet-size distributions of freshly made *n*-tetradecane-in-water emulsions stabilized by (A) gelatin, (B) sodium caseinate, and (C) whey protein isolate (WPI). In the case of gelatin (Fig. 2A), the concentration of approximately 1 wt% protein is close to the optimum concentration for producing fine emulsions (d_{43} = 0.88 μm). Halving or doubling the protein/oil ratio led to emulsions with a substantially greater proportion of large droplets. The poorer emulsifying character of the gelatin at higher concentrations may be a viscosity effect. Sodium caseinate gave increasingly fine emulsions (d_{43} 0.5 μm) as the protein concentration was increased to 2.5 wt% (Fig. 2B), but with no significant improvement above this value. The WPI was found to have an apparently slightly lower optimum protein concentration of 2 wt% (d_{43} = 0.56 μm).

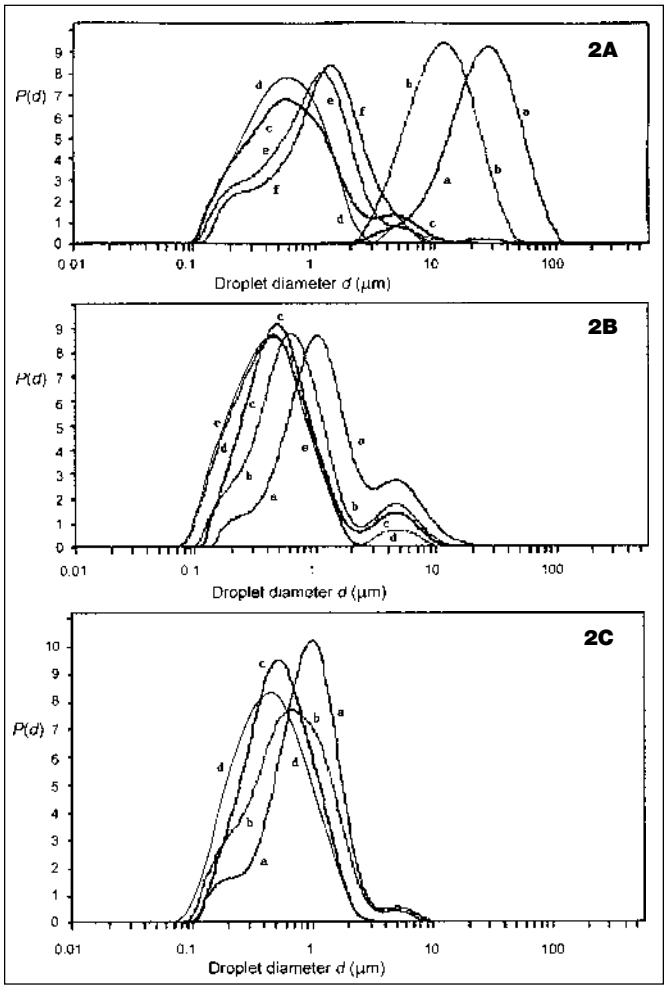

Fig. 2—Droplet-size distributions *P*(*d*) immediately after emulsification for *n*-tetradecane-in-water emulsions (20 vol% oil, pH 6.8, 20 °C) made with different concentrations of the 3 types of protein emulsifier. (A) Gelatin (sample G): (a) 0.25 wt%, (b) 0.5 wt%, (c) 0.75 wt%, (d) 1.0 wt%, (e) 2.5 wt%, (f) 4 wt%. (B) Sodium caseinate (sample C1): (a) 0.25 wt%, (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.0 wt%, (e) 2.5 wt%. (C) Whey protein isolate (sample W3): (a) 0.25 wt%, (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.0 wt%.

Table 3—Effect of centrifugation (2 × 10⁴ *g*, 30 min) and surfactant addition (2 wt% Tween 20) on average droplet size in *n*-tetradecane oil-in-water emulsions (20 vol% oil, 0.5 wt% protein, pH 6.8, 20 °C) made with 3 types of protein emulsifier

Protein emulsifier	Average droplet dia d_{43} (μm)			
	immediately after emulsion formation	after emulsion formation and surfactant addition	following centrifugation	following centrifugation and surfactant addition
gelatin (G)	3.5	1.9	12	10
sodium caseinate (C1)	1.2	1.1	1.1	1.1
whey protein isolate (W3)	0.9	0.8	3.6	0.8

In order to compare more sensitively the emulsifying efficiency of the 3 types of proteins, there is benefit in considering emulsions prepared at constant low protein/oil ratio. Table 3 shows changes in the average droplet size of *n*-tetradecane-in-water emulsions (20 vol% oil, 0.5 wt% protein) following centrifugation and/or surfactant addition. In terms of initial average size, we see that the relative efficiencies of the samples lies in the order W3 > C1 >> G. The highly flocculated state of the freshly made gelatin-stabilized emulsion was indicated by the nearly 50% reduction in d_{43} following surfactant addition, in contrast to the barely significant change in d_{43} for the equivalent caseinate and WPI. Even at this low protein/oil ratio, the caseinate-based emulsion was impressively stable toward centrifugation, which is consistent with its good creaming stability (10 mm serum thickness after 2 wk). In contrast, the relatively coarse gelatin-based emulsion creamed rapidly (32 mm serum thickness after 4 d) and was unstable toward droplet coalescence in the centrifuge (d_{43} increased 3-fold). Although the whey protein-coated droplets were initially rather smaller than the caseinate-coated droplets, the whey protein emulsion creamed considerably faster on extended storage (16 mm serum thickness after 1 wk). This can be explained in terms of the flocculation occurring after emulsion formation through interdroplet disulfide bonding (McClements and others 1993). The sensitivity of the whey protein emulsion to flocculation is well illustrated by the centrifuge test data in Table 3: There was a 4-fold increase in d_{43} following centrifugation that was totally reversed on addition of excess surfactant.

In the presence of 0.5 M NaCl (Table 4), each of the protein types produced *n*-tetradecane droplets of larger average size than in the absence of salt. Although each of the emulsions was affected by centrifugation, the relative performance of the sodium caseinate is distinctly impressive. While there was evidence for some limited flocculation of caseinate droplets following centrifugation, the equivalent gelatin system showed extensive coalescence, and the whey protein system showed both flocculation and coalescence. The results in Table 4 demonstrate the much more effective steric stabilizing behavior of adsorbed caseinate than adsorbed gelatin or whey protein, when compared under interfacial conditions of relatively low surface coverage (that is, low pro-

Table 4—Effect of centrifugation (2 × 10⁴ *g*, 30 min) and surfactant addition (2 wt% Tween 20) on average droplet size in *n*-tetradecane oil-in-water emulsions (20 vol% oil, 0.5 wt% protein, pH 6.8, 20 °C) made with 3 types of protein emulsifier in presence of 0.5 M sodium chloride

Protein emulsifier	Average droplet dia d_{43} (μm)			
	immediately after emulsion formation	after emulsion formation and surfactant addition	following centrifugation	following centrifugation and surfactant addition
gelatin (G)	8.2	15	28	24
sodium caseinate (C1)	1.8	1.5	3.4	2.0
whey protein isolate (W3)	15	1.3	34	13

Table 5—Effect of storage and surfactant addition (2 wt% Tween 20) on average droplet size in *n*-tetradecane oil-in-water emulsions (20 vol% oil, pH 6.8, 20 °C) made with the "optimum" protein concentration for 3 types of protein emulsifier

Protein emulsifier	"Optimum" concentration (wt%)	Average droplet dia d_{43} (μm)			
		immediately after emulsion formation	after emulsion formation and surfactant addition	following storage for 1 wk addition	following storage and surfactant
gelatin (G)	1	0.88	0.62	1.3	0.73
sodium caseinate (C1)	2.5	0.50	nd [a]	0.54	nd [a]
whey protein isolate (W3)	2	0.56	0.48	4.2	0.56

[a] nd = not determined (due to assumed absence of flocculation)

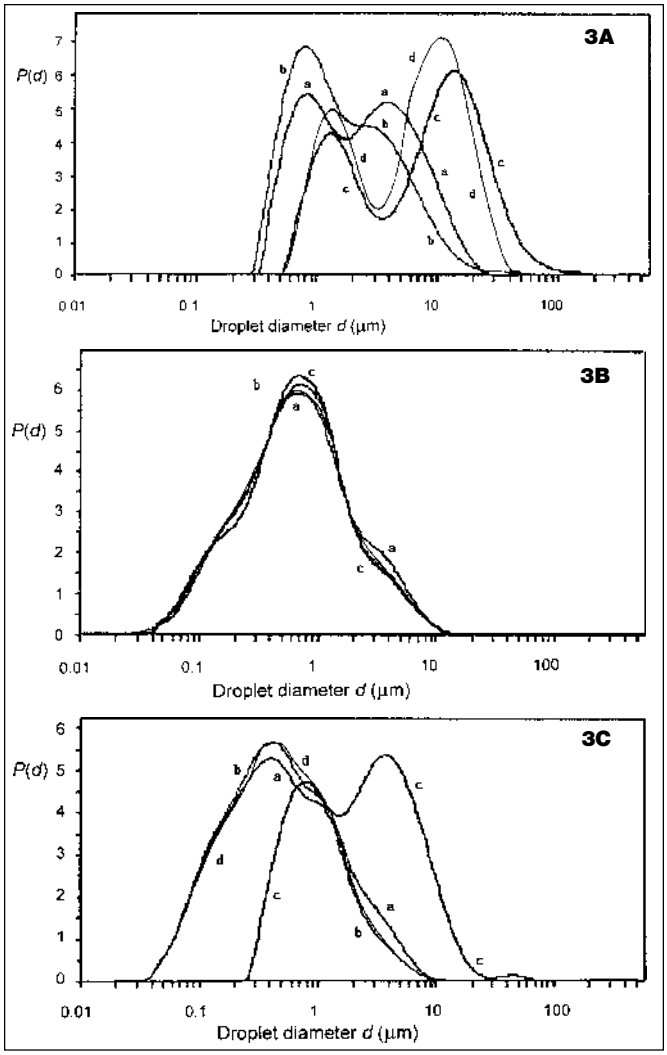

Fig. 3—Effect of centrifugation (2 X 10⁴ *g*, 30 min) and surfactant addition (2 wt% Tween 20) on droplet-size distributions *P(d)* of triglyceride oil-in-water emulsions (20 vol% oil, pH 6.8, 20 °C) for the 3 types of protein emulsifier: (A) gelatin (sample G), (B) sodium caseinate (sample C1), (C) whey protein isolate (sample W3). Key: (a) after emulsification; (b) after emulsification and surfactant addition; (c) following centrifugation and redispersion in phosphate buffer; (d) following centrifugation, redispersion, and surfactant addition.

tein/oil ratio) and solution conditions where electrostatic stabilization is unlikely to make a major contribution (that is, high ionic strength).

Turning now to the triglyceride oil-in-water emulsions, the comparative trends of behavior are similar to the hydrocarbon oil-in-water emulsions, although there are some differences in the detail. Figure 3 presents sets of droplet-size distributions for (a) initial emulsions, (b) after surfactant addition, (c) following centrifugation, and (d) following centrifugation and surfactant addition. The plots in Fig. 3A show that the 0.5 wt% gelatin emulsion was partially flocculated after emulsification and exhibited coalescence on centrifugation. According to Fig. 3B, the 0.5 wt% caseinate emulsion was not flocculated before or after centrifugation and was also stable to coalescence. (Caseinate emulsions can be susceptible to bridging flocculation and coalescence at much lower protein/oil ratios (Dickinson and others 1997).) Figure 3C shows that the 0.5 wt% whey protein emulsion was relatively free from flocculation in its freshly prepared state; subsequent centrifugation led to extensive flocculation but apparently no coalescence.

Finally, let us consider the relative performances of the 3 protein types at their "optimum" concentrations (Table 5). All 3 emulsifiers produced emulsions with submicron-sized droplets. In terms of smallness of initial average droplet dia, and also the maintenance of that dia during storage, the sodium caseinate can be regarded as the most effective emulsifier. Both the gelatin and (especially) the WPI showed evidence of flocculation in the freshly made emulsion and (especially) in the emulsion stored for 1 wk. With none of the emulsifiers was there any indication of significant coalescence during storage. While the WPI appears nearly as effective as the caseinate in terms of initial droplet size, the aggregation of whey-protein-coated droplets during storage clearly has a detrimental effect on the apparent droplet-size distribution and on the associated creaming instability.

Conclusions

THIS STUDY AT NEUTRAL PH HAS SHOWN THAT WHERE FISH gelatin is intended as a replacement for milk protein (especially caseinate), there is benefit in optimizing the protein/oil ratio in order to avoid the presence of large droplets, which may be susceptible to coalescence, especially at high ionic strength. Conversely, where milk protein is intended as

a replacement for gelatin in existing emulsion products, attention should be given to the effect of flocculation of whey-protein-coated droplets on storage.

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