Viscoelastic Properties of Protein-Stabilized Emulsions: Effect of Protein−Surfactant Interactions

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Viscoelastic properties of whey protein isolate-stabilized emulsions have been investigated by determining storage and loss moduli of both fresh emulsions and heat-set emulsion gels. Gel strength increases with the increase of protein concentration in the system. The flocculated protein-covered oil droplets behave as active fillers and hence dramatically enhance the gel strength. The presence of water-soluble surfactant Tween 20 induces a dramatic reduction in emulsion gel strength, which is attributable to protein displacement from the oil−water interface. Oil droplets that are fully covered with Tween 20 do not adhere to protein gel matrix and do not contribute to gel strength. The presence of oil-soluble monopalmitin increases the viscous character of fresh emulsions and substantially reduces the modulus of heat-set emulsion gels. The viscoelastic properties of heat-set emulsion gels containing monopalmitin are only slightly frequency-dependent, and these gels can be classified as "strong gels".

Keywords: *Emulsion gel; whey protein isolate; protein−surfactant interaction; gel strength; Tween 20; monopalmitin glyceride; competitive adsorption*

INTRODUCTION

Food emulsions contain two main classes of surface-active substances that have a strong tendency to adsorb at the oil−water interface—proteins (espcially milk proteins) and small-molecule surfactants (polar lipids). Interactions between proteins and surfactants can be monitored by using various techniques—binding isotherms (Ananthapadmanabhan, 1993), surface/interfacial tension measurement (Le Meste et al., 1997), surface shear rheometry (Chen and Dickinson, 1995a), particle electrophoresis (Chen and Dickinson, 1995b) and specular neutron reflectance (Dickinson et al., 1993a). Small-deformation bulk rheology has also been applied to investigate protein−surfactant interactions in model emulsion gel systems containing heat-set globular proteins (Dickinson and Hong, 1995, 1997; Dickinson et al., 1996).

Globular proteins form gels at sufficiently high concentrations and under conditions of molecular unfolding and aggregation (Ziegler and Foegeding, 1990; Doi, 1993). Among treatments inducing globular protein gelation are heating, high-pressure processing, enzyme action, or urea addition. Addition of calcium ions induces "cold" gelation of whey protein isolate (Hongsprabhas and Barbut, 1997). Oil-in-water emulsions stabilized by globular proteins may also be gelled in various ways—especially by heat treatment (Sternberg et al., 1976; Yamauchi et al., 1980; De Wit, 1984; Jost et al., 1986; Dickinson and Hong, 1995; Wong et al., 1996). Typically, the presence of fine protein-coated oil droplets enhances the strength of the protein network. In general, the textural properties of composite food gels are determined by the combined structural properties of the gel matrix and the filler particles (Tolstoguzov and Braudo, 1983). Strong interaction between filler particles and matrix implies reinforcement of the gel strength. This has been confirmed by microscopy for globular protein emulsion gels. Yost and Kinsella (1992) observed that emulsified butterfat droplets in whey protein isolate gels were intimately associated with the gel protein matrix.

Protein−surfactant interactions have a strong influence on emulsion rheology. In the presence of the nonionic water-soluble surfactant Tween 20 [polyoxyethylene (20) sorbitan monolaurate], the elastic modulus of a heat-set β-lactoglobulin emulsion gel has been found (Dickinson and Hong, 1995) to increase to a maximum at a surfactant/protein molar ratio of $R = 1$ and then to decrease to a minimum at $R = 2$. With the anionic water-soluble surfactant sodium dodecyl sulfate (SDS), there was a slight reduction in modulus at low surfactant additions ($0 < R \leq 2$) followed by a large increase up to a maximum gel strength at $R \approx 6$. In contrast, with the anionic water-dispersible food emulsifier diacetyltartaric acid ester of monoglyceride (DATEM), the gel strength increased continuously with the surfactant concentration (Hong and Dickinson, 1996). Similarly, addition of the zwitterionic surfactant lecithin after emulsification led to an increase in emulsion gel strength with no significant protein displacement from the oil−water interface (Dickinson and Yamamoto, 1996a,b).

Monoglycerides comprise a very important class of food emulsifiers. Previous competitive adsorption experiments have revealed (Dickinson et al., 1993b; Chen and Dickinson, 1993) that oil-soluble surfactants such as monoglycerides are less effective than water-soluble surfactants in displacing milk proteins from the emulsion droplet surface. We report here on the effect of monopalmitin on the small-deformation rheology of whey protein emulsion gels. We consider rheology of triglyceride oil-in-water emulsion systems before and after heat treatment, and we report new data for

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S0021-8561(97)00536-0 CCC: $15.00
Published on Web 01/19/1998

systems containing Tween 20 to facilitate comparison with earlier work.

MATERIALS AND METHODS

Materials. Whey protein isolate PSDI-2400 (PSDI) was obtained from MD Foods Ingredients (Videbaek, Denmark). According to the supplier's specification, the protein content consisted of >95% β-lactoglobulin, the fat content was <1%, and the mineral contents were as follows: Ca, 0.02%; Mg, <0.10%; P, 0.35%; Na, 1.15%. Our analysis of the PSDI sample by fast protein liquid chromatography (FPLC) showed a sharp double peak characteristic of a mixture of the β-lactoglobulin A and B variants. Commercial triolein oil (Trisun 80) was supplied by Danisco (Brabrand, Denmark). The triglyceride fatty acid composition of the oil was as follows: 80% oleic, 9% linoleic, 4% stearic, 4% palmitic. To remove surface-active impurities, the oil was pretreated by passing it through a Florisil column (Gaonkar, 1989). Pure Tween 20 and monopalmitin (Dimodan PA90) were obtained from Sigma Chemicals (Poole, U.K.) and Danisco, respectively. Sigma TRIZMA hydrochloride (Tris-HCl) was used as the buffer solution. The water was double-distilled.

Emulsion Preparation. Protein solutions were prepared in 0.05 M Tris-HCl buffer (pH 7). Oil-in-water emulsions (45 vol % Trisun oil) were made at room temperature using a laboratory-scale jet homogenizer operating at 300 bar. Water-soluble Tween 20 was added to the emulsion after homogenization as required, but for emulsions containing oil-soluble monopalmitin the surfactant was present during homogenization. In this latter case, a known amount of monopalmitin was dispersed in the oil phase at 65−70 °C, and then the oil was cooled to room temperature for emulsification. The emulsion particle-size distribution and specific surface area were determined using a Malvern Mastersizer S2.01.

Protein Surface Concentration. Emulsion samples were centrifuged at $(1.5 \times 10^{-4})g$ for 30 min to separate the oil droplets from the aqueous serum. After passage through a 0.22 mm filter, the aqueous serum was analyzed for protein by FPLC (Dickinson et al., 1989). The surface concentration of whey protein was calculated from the emulsion specific surface area and the difference between the quantity of protein used to make the emulsion and that measured in the serum after centrifugation.

Rheological Measurements. Small-deformation viscoelasticity was investigated by dynamic oscillatory rheometry using a controlled-stress Bohlin CS-50 rheometer. Protein solution or protein-stabilized emulsion (2.5 mL) was carefully poured into a Couette-type cylindrical cell (2.5 cm i.d., 2.75 cm o.d.) and covered with a thin layer of low-viscosity silicone oil to prevent evaporation. Heat-set gelation was induced in situ by heating the sample at constant rate of 3 °C/min from 30 to 85 °C, holding at 85 °C for 35 min, cooling at 1 °C per minute from 85 to 30 °C, and holding at 30 °C for 20 min. Shear rheological properties were determined in the linear viscoelastic region (0.5% strain) with storage and loss moduli measured at a constant frequency of 1 Hz. The storage modulus G' is a measure of the energy stored elastically during an oscillation cycle, and the loss modulus G'' is a measure of the energy dissipated as viscous flow (Tadros, 1996). Some controlled-stress measurements on fresh emulsions and heat-set emulsion gels were also performed as a function of frequency (0.001−10 Hz).

RESULTS AND DISCUSSION

Emulsions without Surfactant. All emulsions made with whey protein isolate PSDI-2400 were found to be stable toward coalescence, but very flocculated ("thick"). Particle-size measurements indicated that the state of flocculation was protein concentration dependent. A maximum in the average particle diameter (d_{32} or d_{43}) was observed for emulsions containing 1−1.5 wt % protein (see Table 1). Figure 1 shows that the fraction of total protein adsorbed at the oil droplet surface, F_p, is a decreasing function of the total protein concentration c_p. We see that only about one-third of the protein resides at the oil droplet surface in the triolein emulsion containing 1 wt % protein. This compares with ∼75% of the available protein adsorbed in a separate emulsion of much finer droplets ($d_{32} = 0.80$ μm) made with 0.85 wt % whey protein and a pure hydrocarbon oil (*n*-tetradecane) (data not shown). The much lower proportion of adsorbed protein in the triglyceride oil-in-water emulsion is attributed to the higher Trisun 80 oil phase viscosity, which leads to larger dispersed droplets, and the greater triglyceride polarity, which reduces the surface coverage (Courthaudon et al., 1991a).

Table 1. Average Particle Size of Fresh Whey Protein-Stabilized Emulsions (45 vol % Trisun, 50 mM Tris-HCl, pH 7.0)[a]

wt % protein	0.55	0.70	1.00	1.50	2.00
d_{32} (μm)	1.95	2.13	2.14	2.19	2.01
d_{43} (μm)	7.9	9.1	10.0	9.7	8.0

[a] Emulsions were made using a laboratory-scale jet homogenizer at 300 bar and room temperature.

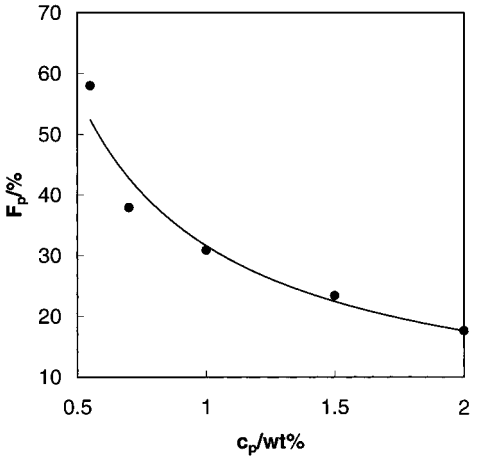

Figure 1. Fraction of whey protein adsorbed at the oil droplet surface in emulsions made with various concentrations of PSDI (45 vol % Trisun, 50 mM Tris-HCl, pH 7). The adsorbed fraction F_p is plotted against the protein concentration c_p.

The emulsion rheological properties are sensitive to total whey protein content. Figure 2 shows that G' exceeds G'' (at 1 Hz) for all of the fresh emulsions, which means that the samples are more elastic than viscous. Both G' and G'' increase initially with increasing protein content and both level off at $c_p \approx 1$ wt %. There is a correlation between the values of the viscoelastic parameters (Figure 2) and the state of flocculation of the emulsions (Table 1), with the maximum values of G' and d_{43} occurring at ∼1 wt % total protein. The increase in elastic modulus associated with the enhanced state of aggregation of the droplets can be understood in terms of the increased effective volume fraction of dispersed phase in the system, since the volume occupied by the aggregates is greater than the sum of the volumes of the contributing particles (van Vliet, 1988).

Typically, emulsions made with whey protein isolates become flocculated as the pH is lowered toward the isoelectric point and the ionic strength increases (Hunt and Dalgleish, 1994; Demetriades et al., 1997). There is a much higher degree of bridging flocculation in the emulsions prepared here at pH 7 and low ionic strength than in those made previously in this laboratory with a sample of whey protein concentrate (WPC) (Dickinson

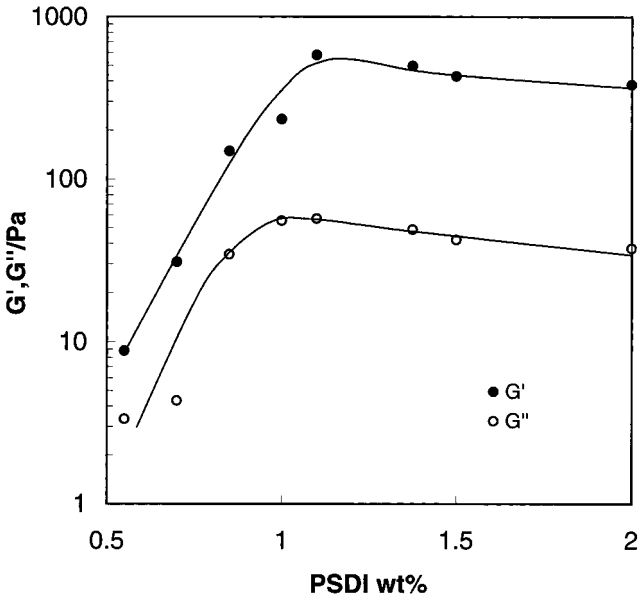

Figure 2. Viscoelastic properties of fresh whey protein-stabilized emulsions (50 mM Tris-HCl, pH 7) containing 45 vol % Trisun. The storage and loss moduli, G' and G'', are plotted against the PSDI concentration in the system: (●) G'; (○) G''.

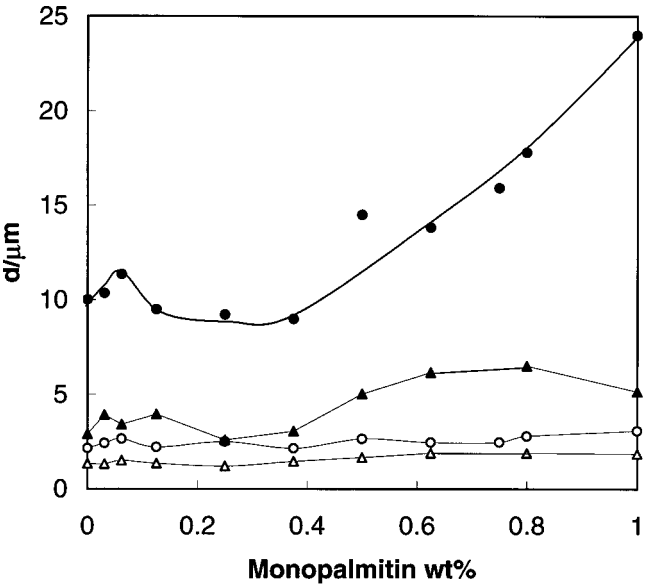

Figure 3. Influence of monopalmitin on effective average particle size of fresh whey protein-stabilized emulsions (1.50 wt % PSDI, 45 vol % Trisun, 50 mM Tris-HCl, pH 7). Average particle diameters d_{32} (○, △) and d_{43} (●, ▲) are plotted against the concentration of monopalmitin: (○, ●) fresh emulsions; (△, ▲) emulsions deflocculated with excess Tween 20.

and Yamamoto, 1996a). A likely explanation is the greater extent of protein aggregation caused by the high concentration of ionic species in the PSDI sample (Hongsprabhas and Barbut, 1997) or by the partially denatured state of the protein induced during whey protein purification and separation.

Emulsions Containing Oil-Soluble Surfactant. The influence of monoglyceride concentration on the average particle size of fresh emulsions containing whey protein isolate plus monopalmitin is shown in Figure 3. We can see that there is a distinct minimum in d_{43} at a monopalmitin concentration of ~0.3 wt %. Qualitatively similar behavior is evident in the d_{32} data, although the relative changes are smaller. The reduced

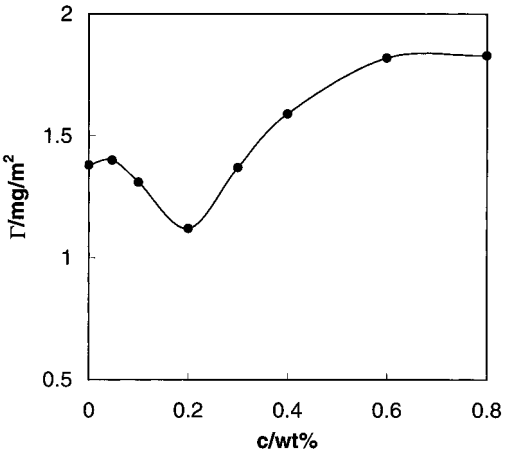

Figure 4. Protein surface coverage in whey protein-stabilized emulsions containing monopalmitin (1.50 wt % PSDI, 45 vol % Trisun, 50 mM Tris-HCl, pH 7). The protein surface concentration Γ is plotted against the monopalmitin concentration c.

stability at monopalmitin concentrations >0.4 wt % may be attributable to surfactant crystallization at the oil droplet surface. Figure 3 also shows the average particle size of the deflocculated systems after treatment of the same emulsions with excess water-soluble surfactant (Tween 20) at a concentration sufficient to displace all of the protein from the oil−water interface. It is assumed that the values of d_{32} and d_{43} for emulsions treated with excess Tween 20 correspond to average sizes of individual droplets, whereas the values for untreated emulsions also include contributions from protein-bridged droplet aggregates. Although the absolute values of d_{32} and d_{43} are lower for the emulsions containing Tween 20, the general trends of behavior are similar, indicating that instability above 0.4 wt % monopalmitin is associated with droplet coalescence rather than just flocculation.

Protein surface coverages have been estimated for emulsions containing whey protein plus monopalmitin using specific surface areas based on the d_{32} values measured in the presence of water-soluble surfactant. Figure 4 shows the protein surface concentration Γ as a function of monopalmitin concentration c. We see that, like other oil-soluble surfactants (Dickinson et al., 1993b), monopalmitin is less effective than water-soluble surfactants in displacing protein from the oil droplet surface. In fact, at high concentrations of monopalmitin, the protein surface coverage is actually even higher than that in the absence of surfactant. The minimum protein surface concentration ($\Gamma = 1.1$ mg m^{-2}) occurs at $c \approx 0.2$ wt %. The explanation for this effect probably involves a couple of interrelated factors. First, the oil-soluble surfactant has a lower capability for displacing protein from the oil droplet surface (Dickinson et al., 1993b). Second, the presence of oil-soluble surfactant at the interface in substantial amounts will tend to destabilize the freshly formed oil droplets during homogenization. This means that the emulsions made at higher concentrations of added monopalmitin have a larger average particle size and a smaller specific surface area. Therefore, as c increases above ~0.2 wt %, more protein becomes available per unit area of droplet surface.

The effect of monopalmitin on the viscoelastic properties of the fresh emulsions is shown in Figure 5. Small additions of surfactant reduce storage and loss moduli

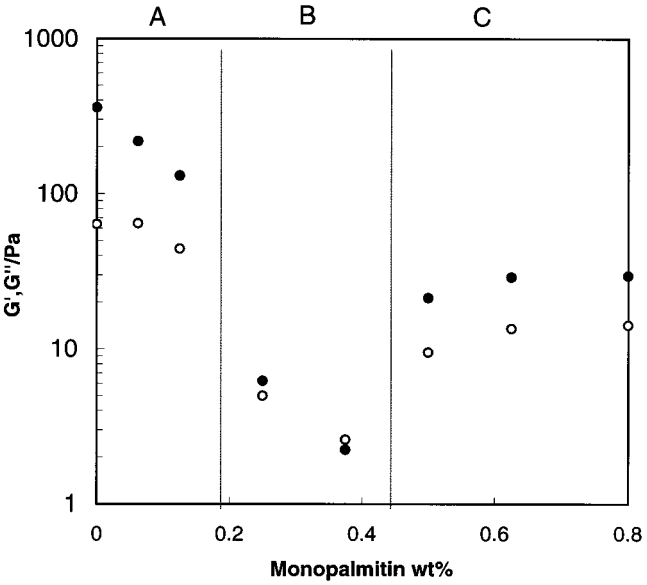

Figure 5. Viscoelastic properties of fresh whey protein-stabilized emulsions (1.50 wt % PSDI, 45 vol % Trisun, 50 mM Tris-HCl, pH 7). The storage and loss moduli, G' and G'', are plotted against the monopalmitin concentration: (●) G'; (○) G''.

to lower values, with minima in G' and G'' reached at $c \approx 0.3$ wt %. Higher monopalmitin concentrations lead to increased moduli, but not so high as for the surfactant-free emulsion. To interpret the data in Figure 5, it is convenient to divide the graph into three regions. Band A refers to very flocculated emulsion droplets with a reasonably high protein surface concentration; the G' and G'' values in this band are only slightly lower than for the pure protein system. The emulsions in band B are of smaller droplet size, are less flocculated, and have a lower protein surface coverage. Being less "structured", these emulsions have lower storage and loss moduli. In band C, the presence of monopalmitin crystals and surfactant−protein interactions at the oil droplet surface leads to an increased protein surface load, enhanced flocculation of coarser droplets, and larger values of the viscoelastic parameters.

The dependence of the rheological parameters on frequency can give information about the types of interactions in the emulsion gel (Almdal et al., 1993). Systems may be usefully classified into "strong gels", "weak gels", and "entanglement networks" (Clark and Ross-Murphy, 1987). The classical strong gel has a permanent (covalent) network, it swells on dilution, and its storage modulus G' is only very slightly frequency-dependent. The entanglement network does not have strong cross-links, it flows like a liquid at low frequencies, and its storage and loss moduli, G' and G'', are highly frequency-dependent, with a "crossover" point occurring at some intermediate frequency. The weak gel has weak "physical" cross-links, it is less frequency-dependent than the entanglement network, and it does not show a crossover point. Figure 6 shows the frequency dependence of fresh emulsions containing 0.7 and 1.5 wt % protein at 30 °C and 0.5% strain. In both cases there is a moderate frequency dependence of the storage modulus with no crossover of G' and G'' over the frequency range. Therefore, these emulsions can be roughly classified as weak gels. Since the protein solution without oil droplets is a dilute Newtonian system, the viscoelastic character of the emulsion must

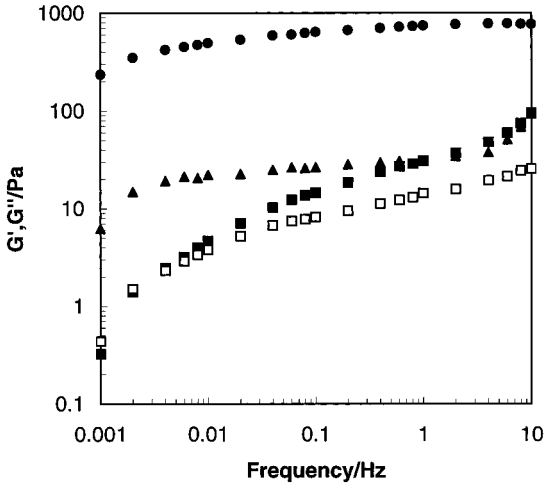

Figure 6. Frequency dependence of storage and loss moduli, G' and G'', of fresh emulsions (45 vol % Trisun, 50 mM Tris-HCl, pH 7) at 30 °C: (●) G', 1.5 wt % PSDI, no monopalmitin; (■) G', 1.5 wt % PSDI, 0.25 wt % monopalmitin; (□) G'', 1.5 wt % PSDI, 0.25 wt % monopalmitin; (▲) G', 0.7 wt % PSDI, no monopalmitin.

arise from the flocculated state of the protein-coated droplets. That is, the pre-emulsified fat droplets are behaving here as active fillers (Ring and Stainsby, 1982).

Figure 6 also compares the frequency dependence of G' and G'' for fresh emulsions in the absence and presence of monopalmitin (0.25 wt %). We see that the moduli for the monopalmitin-containing system are highly frequency-dependent, and there is a crossover in G' and G'' at $\sim 3 \times 10^{-3}$ Hz. When the surfactant content reaches 0.8 wt %, although the emulsion is slightly less frequency-dependent (not shown), the crossover point occurs at a similar frequency. Accordingly, the emulsions containing 0.25 or 0.80 wt % monopalmitin can reasonably be classified as having the rheology of an entanglement gel, whereas the surfactant-free system is more like a weak physical gel. While the reason for this rheological change remains to be clearly established, one might reasonably speculate that, in the presence of monopalmitin, the generation of more protein−lipid interactions at the expense of interfacial protein−protein interactions leads to replacement of many load-carrying connections at the surface of the protein-coated emulsion droplets by a much larger number of weaker interactions (electrostatic, hydrophobic, and hydrogen bonding).

Heat-Set Emulsion Gels. We now consider whey protein emulsion gels prepared by thermal treatment. The time-dependent development of G' and G'' during heating was found to be similar to previous results in our laboratory for β-lactoglobulin or whey protein-stabilized emulsion gels (Dickinson and Yamamoto, 1996a,b). Protein denaturation occurs between 68 °C and 76 °C (depending on protein concentration), which is consistent with the literature (Wong et al., 1996). Figure 7 shows the effect of monopalmitin content on G' and G'' for the final heat-set protein-stabilized emulsion gels at 30 °C. Also shown for comparison are the viscoelastic parameters of heat-set pure protein gels (no droplets). We see that the presence of oil droplets increases the gel strength very dramatically. For instance, to make a protein gel with $G' = 1000$ Pa at pH 7, we need ~10 wt % pure protein solution. However, to make an emulsion gel of same elastic modulus,

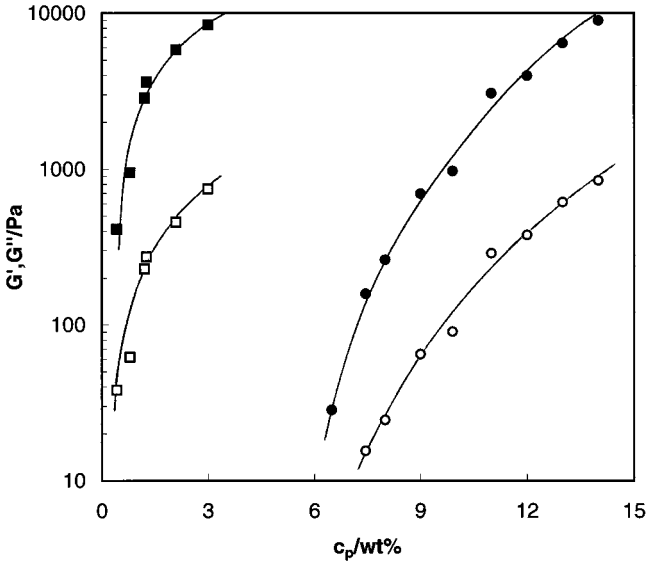

Figure 7. Viscoelastic properties of heat-set protein gels and heat-set protein-stabilized emulsion gels (45 vol % Trisun, 50 mM Tris-HCl, pH 7) at 30 °C. The storage and loss moduli, G' and G'', are plotted against the PSDI concentrations in the aqueous phase: (●) G', protein gel; (○) G'', protein gel; (■) G', emulsion gel; (□) G'', emulsion gel.

Table 2. Viscoelastic Properties of Heat-Set Emulsion Gels Made from Different Source Whey Proteins[a]

system	G' (Pa)	G'' (Pa)
0.70 wt % PSDI, 45 vol % Trisun, pH 7[b]	950	62
3.5 wt % WPC, 45 vol % *n*-tetradecane, pH 7[c]	740	70
7.0 wt % β-lactoglobulin, 45 vol % *n*-tetradecane, pH 7[d]	250	45

[a] The storage and loss moduli, G' and G'', were measured at 1 Hz and 30 °C. [b] This work. [c] Dickinson and Yamamoto (1996a). [d] Dickinson and Yamamoto (1996b).

only ~0.75 wt % protein is necessary! This means that the dispersed oil droplets are very effective space fillers and that they interact very strongly with each other and with the protein gel matrix.

The whey protein sample used in this study produces heat-set protein gels (no droplets) that are rather stronger than those produced with pure β-lactoglobulin alone. For instance, for a protein content of 11 wt %, the storage modulus at 30 °C is 3.1×10^3 Pa as compared with 3.7×10^2 Pa for β-lactoglobulin (Dickinson and Yamamoto, 1996b). However, this difference in gel strength is equivalent to only 1−2 wt % in protein concentration (see Figure 7), whereas the differences in rheological properties of the corresponding emulsion systems are very much more pronounced. Table 2 lists G' and G'' values for heat-set emulsion gels (45 vol % oil) made from β-lactoglobulin and two different sources of whey protein. The PSDI whey protein isolate sample used in these experiments gives stronger emulsion gels than those made previously with 5 times the concentration of WPC (from Armor or DMV) or 10 times the concentration of β-lactoglobulin (Dickinson and Yamamoto, 1996a,b). As these earlier data relate to emulsions made with hydrocarbon oil as the dispersed phase, we have also prepared heat-set protein-stabilized emulsion gels with *n*-tetradecane (45 vol %) and PSDI (0.85 wt %). It was found that G' reached values above 5×10^3 Pa, which shows that the PSDI whey protein produces much stronger emulsion gels than those made previously with β-lactoglobulin or WPC (see Table 2). This difference is presumably mainly attributable to the state of aggregation of the droplets prior to heating. The initial flocculated structure allows the buildup of a strong protein gel matrix during the heat treatment as new molecular bonds are formed between the adjacent aggregated droplets.

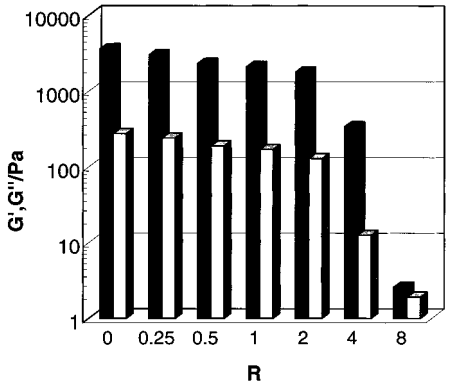

Figure 8. Viscoelastic properties of heat-set emulsion gels with Tween 20 added before heat treatment (1.0 wt % PSDI, 45 vol % Trisun, 50 mM Tris-HCl, pH 7). The storage and loss moduli, G' (solid bars) and G'' (open bars), are plotted against the surfactant/protein molar ratio R.

Systematic displacement of milk proteins from the emulsion droplet surface by the water-soluble surfactant Tween 20 has been demonstrated under a range of experimental conditions (Courthaudon et al., 1991b; Chen and Dickinson, 1993; Dalgleish, 1997), and the implications of this competitive adsorption for the viscoelastic properties of heat-set β-lactoglobulin emulsion gels has been described (Dickinson and Hong, 1995). Figure 8 shows the effect of Tween 20 on the storage and loss moduli of heat-set emulsion gels made with PSDI whey protein. In contrast to the β-lactoglobulin emulsion gel behavior, we observe no dramatic change in viscoelastic properties for surfactant/protein molar ratios less than $R = 2$. There is a steady systematic reduction in G' and G'' with increasing Tween 20 concentration, which becomes especially pronounced for $R \geq 4$. The emulsion gel with $R = 8$ has $G' < 3$ Pa, which corresponds to a gel strength more than 10^3 times weaker than that of the system without added Tween 20. The large difference in behavior from that reported previously for β-lactoglobulin plus Tween 20 emulsion gels suggests differences in competitive adsorption behavior and protein−surfactant interactions for the two systems. Our present results imply that, with increasing surfactant concentration, the oil droplets become less and less strongly incorporated into the network. The strength of adhesion between the surface of filler particles and matrix is a very important factor in determining the rheology of filled gels, and it is known that an enhancement of matrix rigidity occurs only when there is good adhesion between droplets and matrix molecules (Nielsen, 1967). Therefore, it is reasonable to infer that the presence of Tween 20 weakens the interaction of oil droplets with the surrounding protein gel matrix due to loosening of the adsorbed layer structure and partial displacement of protein from the oil−water droplet (Courthaudon et al., 1991b). Oil droplets completely coated with Tween 20 act as inactive space fillers.

The competitive adsorption of PSDI whey protein and Tween 20 at the oil droplet surface in the fresh untreated emulsion has been investigated. (We are unable to determine the protein surface coverage in the

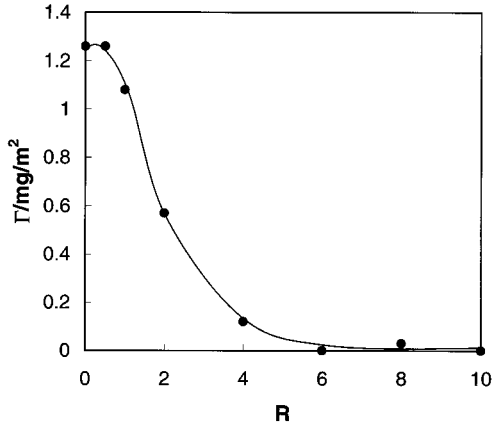

Figure 9. Competitive adsorption of Tween 20 and PSDI at the oil droplet surface in oil-in-water emulsions (1.0 wt % PSDI, 45 vol % Trisun, 50 mM Tris-HCl, pH 7). The protein surface concentration Γ is plotted against the surfactant/protein molar ratio *R*.

final emulsion gel.) Figure 9 shows the protein surface concentration in emulsions before gelling at various values of the molar ratio *R*. Complete displacement occurs for R ≥ 6 (i.e. Tween 20 concentration ≥0.40 wt %). While no significant protein displacement occurs for $R < 1$, we see that at $R = 2$ the protein surface concentration has decreased to about half its original value, which suggests that oil droplets are about half-covered with protein. At $R = 4$, although most of the protein has been displaced from the oil droplet surface in the untreated emulsion (Figure 9), the G' value of the resulting heat-set emulsion gel is still high (~340 Pa). This could mean that, even though the oil droplets are only partially covered by protein, they still have good ability to interact with the gel matrix. A more plausible explanation, however, is that there is substantial increase in the surface concentration of denatured whey protein during the thermal treatment (Dickinson and Hong, 1994).

Viscoelastic properties of heat-set emulsion gels containing various concentrations of monopalmitin have also been determined (Figure 10). For systems containing <0.05 wt % monopalmitin, there is no significant effect on G' and G''. At higher surfactant concentrations, the moduli decrease monotonically with increasing monopalmitin concentration and values appear almost to level off at higher concentrations. At 0.8 wt % monopalmitin (corresponding to $R \approx 30$) the value of G' still exceeds 10^3 Pa. This means that the emulsion droplets containing monopalmitin behave more like active filler particles that interact effectively with the protein network in the aqueous phase. The frequency dependence of G' for heat-set emulsion gels containing 0, 0.25, and 0.80 wt % monopalmitin is shown in Figure 11. In contrast to the fresh emulsion gels (see Figure 6), the presence of monopalmitin does not induce any significant change in the frequency dependence of the viscoelastic parameters. As the behavior is only slightly frequency-dependent, the monopalmitin-containing heat-set emulsion gels can reasonably be described as "classical" strong gels.

This study has shown that rheologically strong emulsion gels of very low protein content can be formulated by thermal treatment of flocculated emulsions of high oil content made with a low concentration of whey protein isolate as sole emulsifier. Moderate addition of monopalmitin has been shown to lead to a substantial

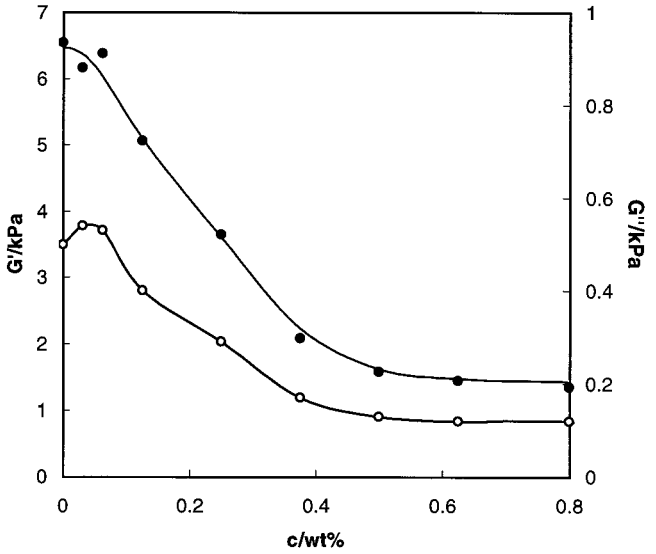

Figure 10. Viscoelastic properties of heat-set emulsion gels containing monopalmitin (1.50 wt % PSDI, 45 vol % Trisun, 50 mM Tris-HCl, pH 7) at 30 °C. The storage and loss moduli, G' (●) and G'' (○), are plotted against the monopalmitin concentration *c*.

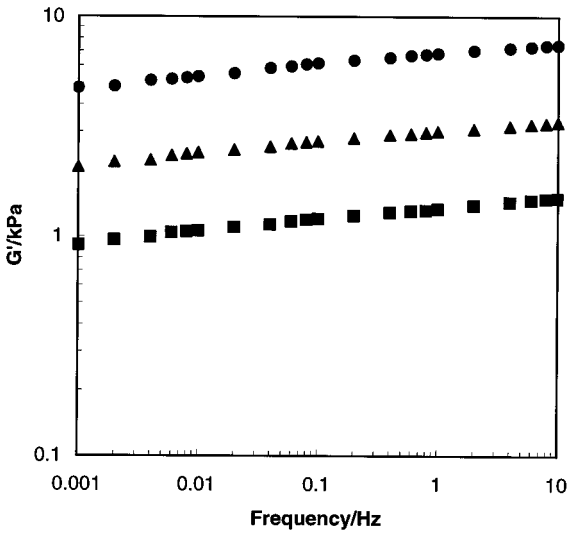

Figure 11. Frequency dependence of elastic modulus of heat-set emulsion gels (1.50 wt % PSDI, 45 vol % Trisun, 50 mM Tris-HCl, pH 7) at 30 °C. The storage modulus G' is plotted against the frequency: (●) no monopalmitin; (▲) 0.25 wt % monopalmitin; (■) 0.80 wt % monopalmitin.

reduction in the elastic modulus, but the effect is very much less than with the water-soluble surfactant Tween 20. The different influences of Tween 20 and monopalmitin on the emulsion gel strength reflect the different interaction mechanisms of water-soluble surfactant and oil−soluble surfactant with protein at the oil−water interface. Whereas the adsorbed protein in the untreated emulsion is completely displaced from the oil−water interface by Tween 20, the protein surface concentration in the equivalent monopalmitin-containing emulsion is actually increased for large surfactant additions.

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Received for review June 23, 1997. Revised manuscript received October 24, 1997. Accepted October 31, 1997. This research was supported by Contract FAIR-CT96-1216 of the European Commission Framework IV Programme.

JF970536C