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Influence of Competitive Adsorption on Flocculation and Rheology of High-Pressure-Treated Milk Protein-Stabilized Emulsions

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The effect of high-pressure treatment (HPT) on the droplet-size distribution and small-deformation rheology of oil-in-water emulsions containing β-lactoglobulin and a nonionic surfactant or sodium caseinate has been investigated at neutral pH. Addition of Tween 20 (polyoxyethylenesorbitan monolaurate) to a β-lactoglobulin-stabilized emulsion results in competitive displacement of the adsorbed globular protein film and, following HPT, the formation of a less flocculated emulsion. The age of the β-lactoglobulin-stabilized emulsion prior to addition of sodium caseinate influences the competitive adsorption behavior. The strengthening of the β-lactoglobulin layer with time makes it more resistant to disruption by sodium caseinate. The level of pressure-induced flocculation of β-lactoglobulin-coated oil droplets depends on the intensity of processing conditions and on the degree of interfacial displacement. In contrast, β-lactoglobulin added after emulsification appears to show little evidence of competitive adsorption behavior at the caseinate oil−water interface. Changes in the rheological properties of these latter systems following HPT can be attributed to pressure-induced denaturation and gelation of β-lactoglobulin in the continuous phase of the emulsion.

Keywords: *High-pressure treatment; oil-in-water emulsions; competitive adsorption; β-lactoglobulin; flocculation; emulsion stability; rheology*

INTRODUCTION

We have reported recently (Dickinson and James, 1998) on the substantial effect of high-pressure treatment (HPT) on the flocculation and rheological behavior of pure β-lactoglobulin-stabilized oil-in-water emulsions. However, many whey protein-based emulsion systems also contain additional surface-active species such as small-molecule surfactants and other milk proteins (caseins). These other species may interact with β-lactoglobulin or compete with it for the oil−water interface; the effects may occur before, during, or after high-pressure processing. To investigate the influence of such effects, this paper explores the influence of HPT on the properties of emulsions containing a mixture of β-lactoglobulin plus nonionic surfactant, Tween 20 (polyoxyethylenesorbitan monolaurate), or a mixture of β-lactoglobulin plus sodium caseinate. Attention is particularly directed toward the effect of the additional surface-active species (Tween 20 or the second milk protein), introduced after emulsification, on the shear rheological behavior of the emulsion prepared with the first milk protein (β-lactoglobulin or sodium caseinate).

The competitive adsorption behavior of proteins and surfactants at the oil−water interface is dependent on the type of surfactant (Dickinson, 1991; Dickinson and McClements, 1995). At high surfactant/protein molar ratios, a nonionic water-soluble surfactant (such as Tween 20) is able to displace completely the adsorbed milk protein from the oil droplet interface. This displacement phenomenon is well recognized for the β-lactoglobulin plus Tween 20 system at both the oil−water interface (Clark et al., 1993; Courthaudon et al., 1991a,b; Mackie et al., 1993; Wilde and Clark, 1993) and the air−water surface (Kragel et al., 1995; Wilde and Clark, 1993). It has been suggested (Chen et al., 1993) that aging of a β-lactoglobulin-stabilized emulsion leads to an increase in the resistance of the adsorbed protein film to interfacial displacement by Tween 20. Competitive displacement by Tween 20 during the thermal gelation of β-lactoglobulin-stabilized emulsions has been found to cause a reduction in gel strength (Chen and Dickinson, 1998; Dickinson and Hong, 1995; Dickinson et al., 1996).

Competitive adsorption between two or more different milk proteins at the oil−water interface is less reversible than that between milk proteins and surfactants (Dickinson, 1994; Dickinson et al., 1990). By “reversibility” we mean here the extent to which the surface composition is independent of the order of introduction of the components to the droplet surface. The interfacial competition in the mixed β-casein plus β-lactoglobulin system is representative of most oil-in-water emulsions containing at least one globular protein (Dalgleish et al., 1991). A useful general rule is that the first protein to adsorb at the interface (e.g., during emulsification) will tend to remain there during storage or further processing. However, the presence of Tween 20 apparently enhances the ability of the milk proteins to exchange between adsorbed and unadsorbed states (Courthaudon et al., 1991b). In mixed whey protein emulsion systems, the presence of Tween 20 during emulsification enables α-lactalbumin to adsorb preferentially at the oil−water interface (Dalgleish et al., 1991). This may be explained in terms of surfactant−β-lactoglobulin complexation (Coke et al., 1990), and it is prevented if the two whey proteins are allowed sufficient time in the adsorbed state.

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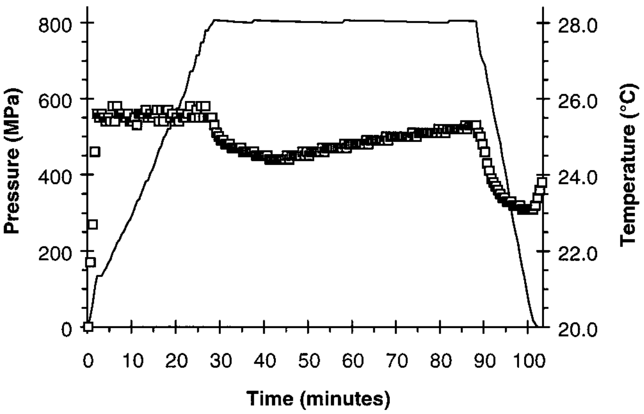

Figure 1. Change in pressure (—) and temperature (☐) during a typical HPT run at a set treatment pressure of $P_{max} = 800$ MPa for 60 min.

MATERIALS AND METHODS

Reagents and Chemicals. The β-lactoglobulin (3× crystallized, lyophilized, L-0230, lot 114H7055), imidazole, research-grade *n*-tetradecane, and Tween 20 were purchased from Sigma Chemical Co. (St. Louis, MO). The sodium caseinate (5.2% moisture, 0.05% calcium) was supplied by Unilever Research, Colworth Laboratory (Bedford, U.K.).

Emulsion Preparation. Contents of emulsifier (protein or surfactant) and oil are expressed as percentages by weight and volume, respectively, of the final mixed emulsion. Oil-in-water emulsions (20 mmol dm^{-3} imidazole buffer, pH 7.0) were prepared with 1.0 wt % β-lactoglobulin, together with 40 vol % *n*-tetradecane, using a laboratory-scale high-pressure Shields homogenizer working at an operating pressure of 40 MPa. Immediately after emulsification (within 1 min), sodium caseinate (0.1−2.0 wt %) or Tween 20 (0.01−4.0 wt %) was added in solution to separate emulsion aliquots. Each emulsion was mixed in an identical fashion by gently inverting the sample container a few times.

The influence of aging of the interfacial β-lactoglobulin film was investigated by altering the time period between emulsion preparation and the addition of sodium caseinate or Tween 20. Emulsions prepared with β-lactoglobulin were stored at 7 ± 2 °C for 6 or 24 h before being mixed with selected solutions of sodium caseinate (0.2 or 1.0 wt %) or Tween 20 (0.5 or 2.0 wt %).

In a second series of experiments, the order of incorporating the two protein components was reversed. That is, emulsions initially prepared with sodium caseinate were mixed with solutions of β-lactoglobulin (0.1−4.0 wt %) to give systems containing 2.0 wt % caseinate and 40 vol % oil. Droplet-size distributions of freshly prepared emulsion samples in all of the experiments were determined using a Malvern Mastersizer MS20 laser light-scattering particle size analyzer (presentation code 0405).

High-Pressure Treatment. Emulsion samples (6 mL) were hermetically sealed in polyethylene bags and subjected to HPT at 200−800 MPa for 5 or 60 min in a laboratory-scale high-pressure processor (Stansted Fluid Power Ltd., Stansted, U.K.). During pressure increase and decrease, the changing temperature in the fluid closely surrounding the bag was continuously monitored. Temperature excursions arising from adiabatic heating/cooling were prevented by carefully controlling the rates of compression/decompression (Dickinson and James, 1998). Therefore, the permitted temperature range was kept at 20−26 °C during periods of compression and decompression while the temperature was maintained at 25 ± 1 °C during the holding period at the set treatment pressure. A typical pressure/temperature profile is provided in Figure 1 for the most intense HPT run considered (i.e., a set pressure of 800 MPa with a 60 min holding time).

Pressure-treated samples were characterized with respect to oil droplet-size distribution and rheological behavior. No ultrasonication was applied to samples prior to particle-size determination, but samples were stirred gently to an equivalent degree to facilitate dispersion in the Mastersizer tank. Untreated mixed emulsions were also analyzed immediately after preparation and again following a period of storage at 25 ± 1 °C for a length of time equivalent to that of the pressure treatment (ca. 1 and 2 h for HPT times of 5 and 60 min, respectively). To compare HPT processes with the same treatment time but with different maximum pressures, the time intervals between *mixed* emulsion preparation (i.e., following addition of the second species) and flocculation/rheology analysis (following HPT) should be the same. For each set treatment pressure, mixed emulsion samples were therefore stored at 25 ± 1 °C for appropriate lengths of time, prior to HPT, to account for differences in the duration of compression and decompression.

Emulsion Rheology. High-pressure-treated emulsions (and untreated emulsions of the same age) were characterized in terms of their rheological properties. The viscosity of samples was sufficiently low to allow easy transfer of treated emulsions into the rheometer cell without significant disruption of structure or influence on subsequent rheological measurements. Small-deformation shear viscoelastic measurements (strain < 0.5%) were made using a controlled stress Bohlin CS-50 rheometer with a concentric cylindrical cell (inner diameter = 14 mm, outer diameter = 15.4 mm, sample volume = ~2 mL). Oscillatory experiments were conducted at 25.0 ± 0.5 °C, and the complex shear modulus (G^*) was recorded at the arbitrarily chosen reference frequency of 0.01 Hz. All experiments were repeated at least once, and error bars on points indicate standard deviations about the mean for the whole set of measurements.

RESULTS AND DISCUSSION

Emulsion stability has been characterized in terms of changes in the average particle size parameter

$$d_{43} = \sum_i n_i d_i^4 / \sum_i n_i d_i^3$$

where n_i is the number of droplets of diameter d_i. The d_{43} value for the freshly prepared emulsion represents the average size of the primary (unflocculated) emulsion droplets. Changes in d_{43} for stored and pressure-treated emulsions reflect changes in the effective particle size. (The word “effective” is used here because the changes are predominantly due to aggregation of the primary droplets and not to their coalescence.) As reported previously for the pure β-lactoglobulin-stabilized emulsions (Dickinson and James, 1997, 1998), HPT induces an increase in the level of flocculation as indicated by an increase in the effective average droplet size and an associated increase in viscoelasticity. The average droplet diameter d_{43} increases from 0.55 ± 0.04 to 1.08 ± 0.10 μm and the complex modulus G^* from 0.003 ± 0.001 to ~3 Pa following treatment for 60 min at a pressure of 800 MPa.

The addition of sodium caseinate to the aqueous continuous phase causes a significant change in the observed pressure dependence of the state of aggregation of the β-lactoglobulin emulsions. Increasing the added amount of this second protein reduces the extent of pressure-induced flocculation, as indicated by the reduction in d_{43} (Figure 2) and G^* (Figure 3). At caseinate concentrations >0.5 wt %, the emulsion properties are no longer affected by HPT.

The behavior of the β-lactoglobulin plus Tween 20 emulsions with HPT appears to resemble that of the β-lactoglobulin plus caseinate systems. In the presence of Tween 20, the β-lactoglobulin-stabilized emulsions

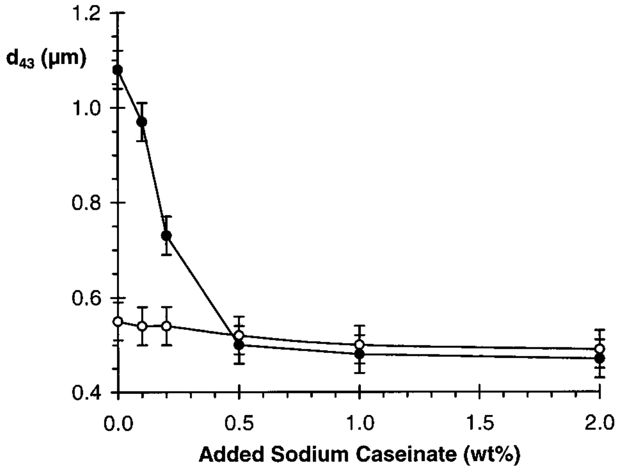

Figure 2. Influence of sodium caseinate addition on the average droplet diameter d_{43} of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin following ambient quiescent storage (~2 h) (○) and HPT for 60 min at 800 MPa (●). Error bars represent standard deviation about the mean.

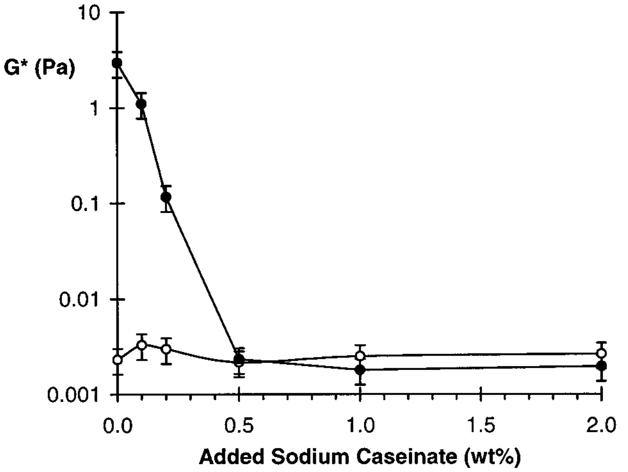

Figure 3. Influence of sodium caseinate addition on the complex modulus G^* (at 0.01 Hz, 25 °C) of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin following ambient quiescent storage (~2 h) (○) and HPT for 60 min at 800 MPa (●). Error bars represent standard deviation about the mean.

become less affected by HPT as again indicated by the reduction in average droplet size (Figure 4) and the reduction in gel strength (Figure 5). At added concentrations of Tween 20 of ≥2 wt %, the HPT has a negligible effect on the extent of flocculation.

The data in Figures 2–5 can be explained in terms of competitive displacement of the β-lactoglobulin emulsifier from the oil–water interface by sodium caseinate or Tween 20 before or during the HPT. The displaced globular protein is not available for cross-linking between surfaces of adjacent emulsion droplets, and hence the effect of the added displacer is to reduce the extent of flocculation as detected by the d_{43} and G^* data.

A previous study has shown (Dickinson and Matsumura, 1991) that gradual strengthening of the β-lactoglobulin film following emulsion preparation occurs through formation of interfacial intermolecular disulfide bonds at the interface. It is possible that, prior to the addition of a second more surface-active species, film strengthening may lead to an increase in the resistance of the adsorbed β-lactoglobulin layer to competitive displacement. Hence, it seemed interesting to investigate the influence of aging time on the effect of Tween 20 or sodium caseinate on β-lactoglobulin emulsion flocculation after HPT. Comparing effects of HPT in emulsions of different ages is complicated by the occurrence of gradually increasing levels of flocculation during quiescent storage at ambient temperatures and pressures (McClements et al., 1993), and therefore to the problem of different potential initial droplet-size distributions (before HPT). Making allowance for this phenomenon, the percentage rise in average droplet size following HPT was found to be reasonably consistent (90 ± 5%) for each of the aged, control samples (containing only β-lactoglobulin).

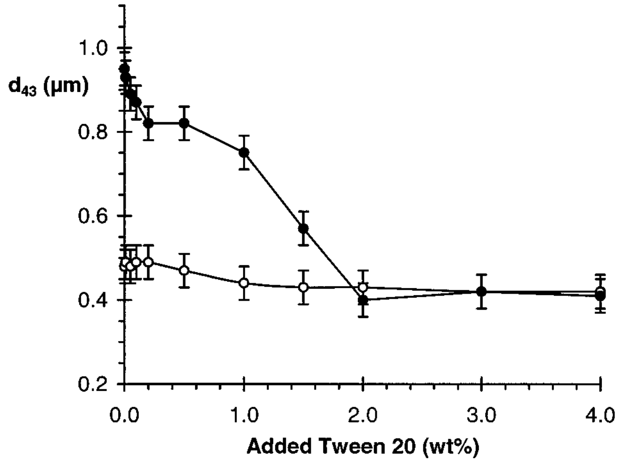

Figure 4. Influence of Tween 20 addition on the average droplet diameter d_{43} of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin following ambient quiescent storage (~2 h) (○) and HPT for 60 min at 800 MPa (●).

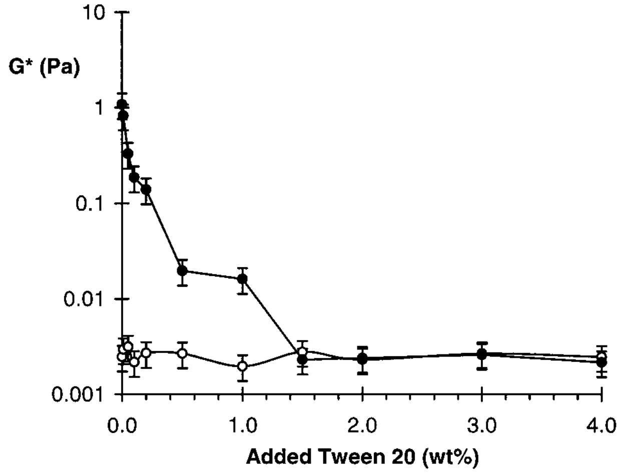

Figure 5. Influence of Tween 20 addition on the complex modulus G^* (at 0.01 Hz, 25 °C) of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin following ambient quiescent storage (~2 h) (○) and HPT for 60 min at 800 MPa (●).

The data in Table 1 suggest that aging of the β-lactoglobulin-stabilized emulsion (for up to 24 h) has a negligible influence on the change in average droplet size caused by the presence of Tween 20, added prior to HPT. Therefore, the susceptibility of adsorbed β-lactoglobulin molecules to interfacial displacement by surfactant during HPT appears unchanged, in contrast to behavior without HPT reported previously (Chen et al., 1993). However, the same behavior was not found with sodium caseinate replacing Tween 20. In this case, aging

Table 1. Effect of Aging Time following Preparation of Emulsions (40 vol % Oil, pH 7.0, 1.0 wt % β-Lactoglobulin) and Addition of Tween 20 or Sodium Caseinate prior to HPT (800 MPa for 60 min) on the Final Average Droplet Diameter d_{43}

	d_{43} (μm)					
	immediate addition		addition after 6 h		addition after 24 h	
concn (wt %)	untreated	treated	untreated	treated	untreated	treated
0, sodium caseinate	0.55 ± 0.04	1.08 ± 0.10	0.59 ± 0.05	1.12 ± 0.16	0.68 ± 0.05	1.26 ± 0.18
0.2, sodium caseinate	0.54 ± 0.04	0.73 ± 0.07	0.58 ± 0.05	1.04 ± 0.10	0.65 ± 0.05	1.11 ± 0.14
1.0, sodium caseinate	0.50 ± 0.04	0.48 ± 0.04	0.58 ± 0.05	0.85 ± 0.07	0.66 ± 0.05	0.99 ± 0.10
0, Tween 20	0.48 ± 0.04	0.95 ± 0.10	0.56 ± 0.05	1.07 ± 0.12	0.64 ± 0.05	1.23 ± 0.20
0.5, Tween 20	0.47 ± 0.04	0.82 ± 0.08	0.57 ± 0.05	0.90 ± 0.08	0.63 ± 0.05	0.95 ± 0.10
2.0, Tween 20	0.43 ± 0.04	0.40 ± 0.04	0.56 ± 0.05	0.47 ± 0.04	0.61 ± 0.05	0.48 ± 0.04

was found to result in a significantly different effect of HPT on the change in average droplet size caused by the presence of sodium caseinate. A smaller fall in d_{43} upon aging suggests that caseinate competes less well for the oil–water interface when the β-lactoglobulin has been allowed time to restructure and cross-link in the adsorbed state. It is also possible that HPT causes the nonionic surfactant to become a more efficient displacer due to some change in the surfactant self-association behavior or in the nature of the protein–surfactant interactions.

The presence of a sufficient quantity of Tween 20 or sodium caseinate (added immediately after emulsification) causes significant reduction in the degree of pressure-induced flocculation of the β-lactoglobulin-stabilized emulsion. At sufficiently high concentrations of added Tween 20 or sodium caseinate, the mixed emulsions become unaffected by HPT. By directly comparing the value of this *critical* concentration for the most intense treatment (800 MPa for 60 min) with that for less intense treatments, we can explore the extent to which the competitive adsorption behavior is influenced by the nature of the HPT conditions.

Treatment at a pressure of 200 MPa for holding times of 5 and 60 min was found to have a negligible effect on the properties of β-lactoglobulin-stabilized emulsions, even in the absence of an interfacial competitor. For this reason, results for treatments at this low pressure have been excluded from the discussions that follow. Subjecting β-lactoglobulin-stabilized emulsions (without Tween 20) to HPT ($\geq$400 MPa) induces increases in d_{43} and G^* that are sensitive to the maximum applied pressure and the treatment time. The addition of increasing amounts of Tween 20 causes a gradual reduction in average droplet size following HPT for 5 min (Figure 6) or 60 min (Figure 7). At sufficiently high Tween 20 concentrations (>2 wt %), the extent of emulsion flocculation appears unaffected by HPT. The associated reduction of the complex modulus follows a similar trend on treatment at different pressures for 5 or 60 min (Figures 8 and 9), although the situation of a negligible change in G^* becomes apparent at an even lower surfactant concentration.

As expected, then, the extent of the pressure-induced change in emulsion properties is determined by the length and severity of the treatment conditions. In accordance with previous findings [see, for example, Mackie et al. (1993)], the Tween 20 appears to displace β-lactoglobulin from the oil–water interface. The degree of interfacial displacement is dependent on the relative amount of surfactant present. The fact that Tween-20-coated oil droplets are unaffected by pressure accounts for the reduction in the level of flocculation with increasing surfactant concentration. At a sufficiently high surfactant/protein ratio, the values of the parameters d_{43} and G^* are unaffected by HPT because the oil–water interface is predominantly coated with surfactant.

These findings demonstrate the potential for controlling the extent of pressure-induced flocculation in β-lactoglobulin emulsions by altering both the intensity of HPT and the degree of protein displacement. Therefore, combining HPT with the competitive adsorption phe-

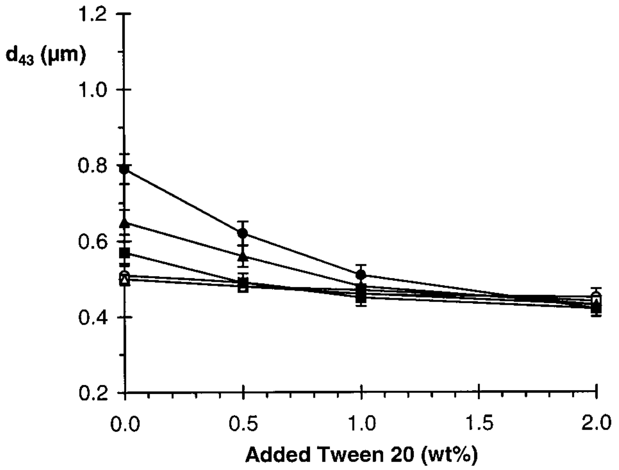

Figure 6. Change in the average droplet diameter d_{43} of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin as a function of Tween 20 concentration, following HPT at 800 MPa (●), 600 MPa (▲), and 400 MPa (■) for 5 min and after ambient quiescent storage (~1 h) (corresponding open symbols).

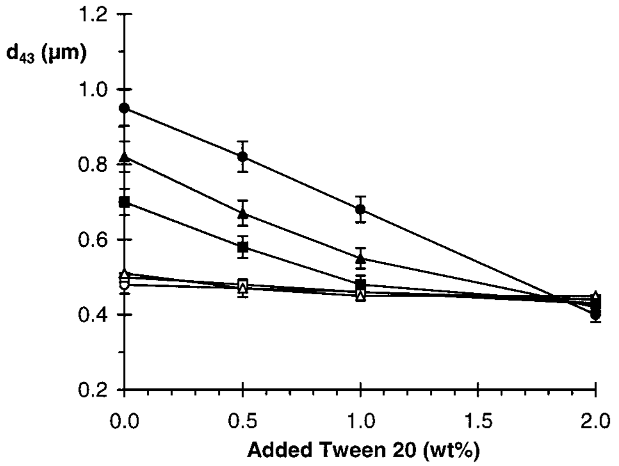

Figure 7. Change in the average droplet diameter d_{43} of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin as a function of Tween 20 concentration, following HPT at 800 MPa (●), 600 MPa (▲), and 400 MPa (■) for 60 min and after ambient quiescent storage (~2 h) (corresponding open symbols).

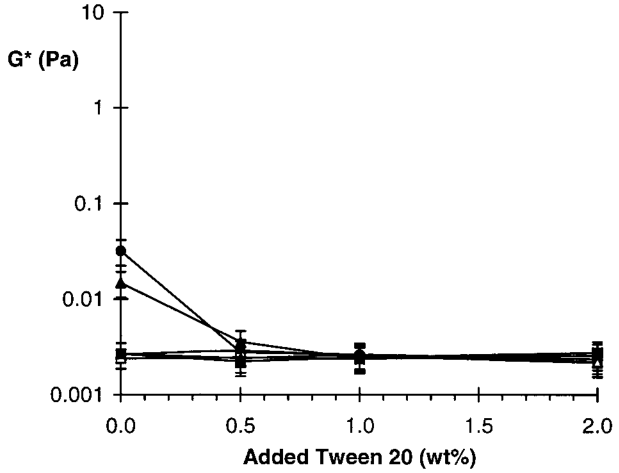

Figure 8. Change in the complex modulus G^* (at 0.01 Hz, 25 °C) of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin as a function of Tween 20 concentration, following HPT at 800 MPa (●), 600 MPa (▲), and 400 MPa (■) for 5 min and after ambient quiescent storage (~1 h) (corresponding open symbols).

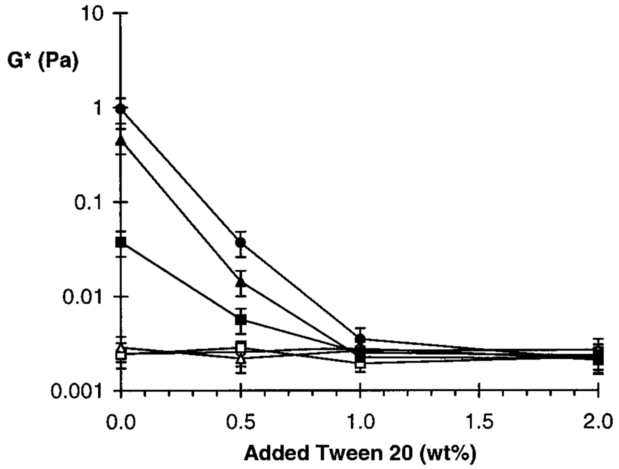

Figure 9. Change in the complex modulus G^* (at 0.01 Hz, 25 °C) of emulsions (40 vol % oil, pH 7.0) stabilized by 1.0 wt % β-lactoglobulin as a function of Tween 20 concentration, following HPT at 800 MPa (●), 600 MPa (▲), and 400 MPa (■) for 60 min and after ambient quiescent storage (~2 h) (corresponding open symbols).

nomenon could represent a processing strategy for controlling emulsion stability in these types of systems.

Negligible changes in average droplet size and complex modulus were observed following intense HPT (800 MPa for 60 min) of emulsions stabilized by sodium caseinate (in the absence of β-lactoglobulin). This serves to confirm the ability of the casein-based system to resist high-pressure processing. This can be attributed to the disordered structure of the protein (Dickinson et al., 1997; Dickinson and James, 1997).

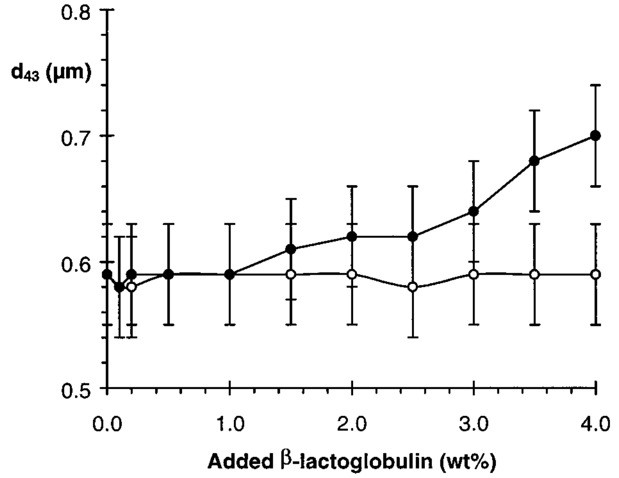

Figure 10. Influence of adding β-lactoglobulin on the average droplet diameter d_{43} of emulsions (40 vol % oil, pH 7.0) stabilized by 2.0 wt % sodium caseinate following ambient quiescent storage (~2 h) (○) and HPT for 60 min at 800 MPa (●).

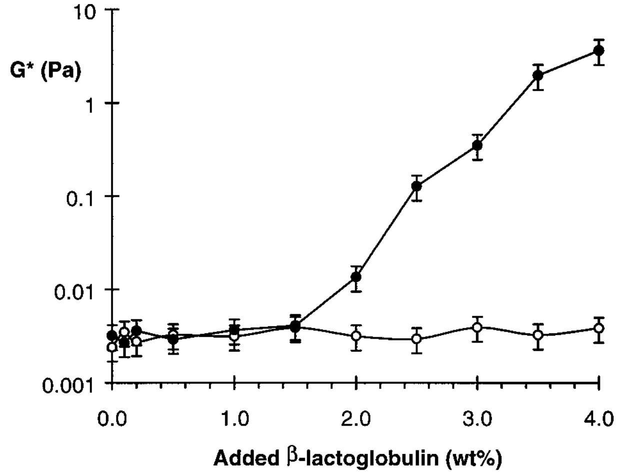

Figure 11. Influence of adding β-lactoglobulin on the complex modulus G^* (at 0.01 Hz, 25 °C) of emulsions (40 vol % oil, pH 7.0) stabilized by 2.0 wt % sodium caseinate following ambient quiescent storage (○) (~2 h) and HPT for 60 min at 800 MPa (●).

There is little evidence from these experiments to suggest that β-lactoglobulin can compete successfully for the oil–water interface in the presence of adsorbed sodium caseinate. Up to ~2.5 wt % β-lactoglobulin, the presence of this added protein was found to have a negligible effect on emulsion flocculation properties following HPT. A very slight increase in the average droplet size is observed at 2–3 wt % β-lactoglobulin (Figure 10), and an increase of ~15% is observed at 4.0 wt % β-lactoglobulin, indicating a low level of oil droplet flocculation at this relatively high level of globular protein addition. Of far greater significance is the substantial rise in complex modulus G^* following HPT at β-lactoglobulin concentrations >1.5 wt % (Figure 11). This enhancement of the emulsion gel strength is clearly not indicative of extensive droplet flocculation (as for the pressure-treated β-lactoglobulin-stabilized emulsions) because of the constancy of the d_{43} values (Figure 10). The explanation presumably lies with modifications to the rheological properties of the continuous phase arising from pressure-induced unfolding and aggregation of the unadsorbed β-lactoglobulin molecules, which results in the formation of a weak gel network in the gaps among the emulsion droplets. Furthermore, the presence of caseinate-stabilized oil droplets, constituting 40% of the system volume, dispersed within this gel-like protein matrix, will no doubt have an additional influence on the overall rheological behavior.

The above results suggest that the application of a high hydrostatic pressure sufficient to unfold the β-lactoglobulin molecules does not lead to any substantial increase in the ability of this globular protein to displace casein from the surface of emulsion droplets. This behavior appears to differ from that arising from the effect of thermal treatment on the casein/β-lactoglobulin competitive adsorption behavior. It has recently been reported by Dalgleish (1999) that casein can be competitively displaced from the oil−water interface by β-lactoglobulin on increasing the temperature to just 50 °C, that is, below the normal denaturation temperature of the protein. Similarly, we have shown recently in our laboratory (unpublished results) that addition of a relatively low concentration of β-lactoglobulin to a concentrated caseinate-stabilized emulsion prior to heat treatment at 85 °C can produce a large change in the rheology of the resulting system (i.e., converting it from a liquid-like emulsion into a strong heat-set gel). This qualitative difference in the effects of HPT and thermal treatment on the interactions and competitive adsorption in emulsions containing mixed milk proteins seems worthy of further systematic investigation.

CONCLUSIONS

The displacement of β-lactoglobulin from the oil−water interface by sodium caseinate and Tween 20 results in a milk protein emulsion system having a state of flocculation that is less dependent on applied hydrostatic pressure.

By allowing β-lactoglobulin time to age at the oil−water interface prior to the addition of the second surface-active protein component, the globular protein film becomes more resistant to displacement by sodium caseinate. In contrast, however, emulsion aging has little influence on the competitive displacement of β-lactoglobulin by added Tween 20 prior to HPT.

Pressure processing does not appear to induce any significant degree of complexation between β-lactoglobulin and sodium caseinate in emulsions stabilized by the latter disordered protein, although very low levels of flocculation are detected. In these systems, pressure-induced denaturation of β-lactoglobulin in the aqueous phase leads to weak gel formation at high concentrations (4 wt %), despite little apparent interaction between droplets.

Overall, these results suggest that the level of pressure-induced flocculation in concentrated whey-protein-stabilized emulsions can be controlled by altering the intensity of the HPT process and by adjusting the amount of interfacial competitor added. Therefore, the principle of combining these two factors can be viewed as a novel way of manipulating the microstructure and texture of dairy emulsion systems.

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