Surface Properties of Oil-in-Water Emulsion Droplets Containing Casein and Tween 60

Douglas G. Dalgleish,*,† Magesh Srinivasan,‡ and Harjinder Singh‡

Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and Department of Food Technology, Massey University, Palmerston North, New Zealand

Studies have been made of changes in the surface properties (thickness of the adsorbed protein layer, ζ-potential) of droplets formed when Tween 60 was incorporated into emulsions prepared from sodium caseinate and soy oil. At molar ratios of surfactant/protein of up to 90:1, Tween displaced some, but not all, of the casein from the interface, the amount depending on the relative concentrations of the two surfactants. Both the thickness of the adsorbed layer of casein and the ζ-potentials of the particles depended strongly on the amount of Tween present, both of these properties becoming smaller in magnitude as the concentration of Tween increased. However, in addition, the layer thickness and the ζ-potential depended on the overall concentration of protein, not simply on the actual amount adsorbed, so that emulsions with the same protein load but different protein concentrations did not show the same surface properties. This behavior can be explained if the Tween not only competes with protein for the interface but causes conformational changes in the protein molecules already adsorbed.

Keywords: *Oil-in-water emulsions; protein adsorption; emulsion structure; protein–surfactant interactions*

INTRODUCTION

It is by now a well-established fact that proteins and small molecule emulsifiers compete for the interface in oil-in-water emulsions (Courthaudon *et al.*, 1991b–d; de Feijter *et al.*, 1987; Wilde and Clark, 1993). Among these, emulsions stabilized by milk proteins in combination with Tweens (polyoxyethylene sorbitan monoesters of fatty acids) have been studied. In these, although the protein may initially be present on the interface, it is partially or completely displaced by the small molecule, depending on the protein/surfactant ratio. In addition, if more than one type of protein is present, the surfactant may enhance the competition of the molecules for the oil–water interface (Courthaudon *et al.*, 1991d). Because the surfaces of the emulsion droplets change as surfactant replaces protein, their properties are altered, since although the small surfactants are capable of lowering the interfacial tension more than are proteins, they weaken the mechanical properties of the interface and, in fact, may lead to enhanced instability of the emulsions (Goff and Jordan, 1989).

In emulsions stabilized by protein alone, the interfacial layer stabilizes the particles in two ways; first, it provides a layer that protrudes from the interface, to a depth of 1–2 nm for whey proteins and of up to 10 nm for caseins (Mackie *et al.*, 1991; Dalgleish, 1993; Fang and Dalgleish, 1993a). This layer provides for steric stabilization, so that close approach of the particles is inhibited. Also, proteins are charged, usually negatively, and so emulsion droplets to which protein is adsorbed acquire a substantial charge (Dickinson *et al.*, 1989). This also may prevent the close approach of the particles, as expressed by the DLVO mechanism. Even if both charge and steric effects are insufficient to prevent the aggregation of the droplets, the presence of a mechanically strong interfacial layer of protein may prevent coalescence.

The displacement of the adsorbed protein by small (uncharged) surfactant destroys all of these stabilizing influences at once. The steric effect is much reduced, because the adsorbed surfactant will protrude less into the solution; the charge stabilization will be decreased, because the surfactant replaces the charged macromolecule, and the aggregated and mechanically strong interfacial layer is weakened by the presence of surfactants that lack a cohesive tendency. Indeed, such emulsions are important in forming structures in whipped toppings and ice creams.

Competition between surfactant molecules, especially proteins, for the interface may depend on the source of the protein. Thus, although purified α_{s1}- and β-caseins compete for the interface (Dickinson *et al.*, 1988), similar experiments involving sodium caseinates (which contain mainly these two proteins) show less tendency to competition (Robson and Dalgleish, 1987; Hunt and Dalgleish, 1994). This is also true when caseinate is used in emulsions mixed with Tween 60; there is only a small preferential adsorption (Euston *et al.*, 1995).

The structure of the interfacial layer of emulsions containing caseinates can be studied by dynamic light scattering (Dalgleish, 1993) combined with analysis of the amounts and types of proteins in the adsorbed layers of emulsions (Hunt and Dalgleish, 1994). These proteins form extended layers, whose structures can be altered by surfactants such as lecithins (Fang and Dalgleish, 1993b), although it has been established that lecithins do not displace caseins readily, in the same way that has been observed for other surfactants (Courthaudon *et al.*, 1991a). It is also possible to use dynamic light scattering combined with particle electrophoresis to measure the apparent ζ-potential of the particle surface, i.e. the apparent charge at the surface

* Author to whom correspondence should be addressed [e-mail ddalglei@uoguelph.ca; fax (519) 824-6631.

† University of Guelph.

‡ Massey University.

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of shear (Dalgleish *et al.*, 1985; Dickinson *et al.*, 1989). These measurements may be combined to give a better picture of the behavior of the interfacial layer as the protein is displaced by the small molecule surfactant.

This paper describes the changing behavior of the interfacial layer in emulsions made using sodium caseinate and soy oil, in which different amounts of the surfactant Tween 60 were incorporated. The effects of the surfactant on the hydrodynamics of the adsorbed layer and on the surface potentials of the emulsion droplets were measured, to attempt to understand how the presence of Tween affects the properties of the emulsion.

MATERIALS AND METHODS

Soy oil, sodium dodecyl sulfate (SDS), Tween 60, and buffer salts were purchased from Sigma Chemical Co., St. Louis, MO. 2-Mercaptoethanol was obtained from Fisher Chemicals, Mississauga, ON. Caseinate (Alanate 180) was provided by the New Zealand Dairy Board, Wellington, New Zealand.

Emulsion Preparation. Oil-in-water emulsions were prepared using a Microfluidizer M110S (Microfluidics Corp., Newton, MA) at an input pressure of 0.3 MPa (corresponding to a homogenization pressure of 42 MPa or 6200 psi), using soy oil (20 wt %) and buffered (20 mM imidazole–HCl, pH 7.0) caseinate solution. Protein concentrations were 0.5, 1.0, and 2.0 wt % in the aqueous phase, and solutions were filtered (0.22 μm pore) prior to homogenization. The ingredients were weighed into a beaker, and a pre-emulsion was made using a hand-held shear-mixing unit (Dia-Med, Mississauga, ON). The pre-emulsion was introduced into the Microfluidizer and was circulated through the unit for 10 strokes of the pump, collected, and then subjected to a further 10 pump strokes before finally being collected. At each concentration of protein, sufficient amounts of Tween 60 were incorporated to give final concentrations of 0, 0.2, 0.4, 0.6, 0.8, and 1%. The Tween was added to the protein/oil/buffer mixtures before the pre-emulsion was made. For comparison purposes, an emulsion was also made containing Tween and no protein. All experiments were conducted at 25 °C.

The emulsions prepared in this way were stable (no change in particle size was detected) over a period of several days, although measurements were generally made within 12 h of the formation of the emulsion.

Determination of Particle Sizes and Particle Size Distribution. The size distribution of the emulsion droplets was determined using a Mastersizer X (Malvern Instruments Ltd., Southboro, MA), with optical parameters defined by the manufacturer's presentation code 0303. Milli-Q water was used as the dispersant, and the dilution factor was approximately 1 in 1000. Changes in the size distributions of the emulsions as the concentrations of Tween and protein are varied have been described in detail (Euston *et al.*, 1995); the protein concentration has some effect (higher protein gives smaller droplets), but the incorporation of Tween into the protein-stabilized emulsions has only a relatively small effect.

Average diameters of the emulsion droplets were measured by photon correlation spectroscopy (PCS) using a Malvern 4700 optical system attached to a 7032 correlator. Measurements were all made at a scattering angle of 90°, and all emulsions were diluted at a ratio of 1.5 μL of emulsion per 3 mL of buffer. The buffer was filtered through a 0.2 μm filter before the emulsion sample was added, but no attempts were made to filter the emulsion before or after dilution, since filtration is known to remove some particles from the suspension. Temperature was maintained at 25 °C. Diffusion coefficients of the particles were calculated by the method of cumulants, and from these hydrodynamic diameters were obtained by assuming that the emulsion droplets were spherical and obeyed Stokes's law. For each sample, repeated sets of 10 individual PCS runs, each lasting 30 s, were made, and then the results were averaged. The average measured spread of results between the averages from the sets of runs was ±2 nm (Fang and Dalgleish, 1993a).

To study the change of emulsion droplet size resulting from the breakdown of the adsorbed layer by proteolytic enzymes, the diameters of the droplets were measured and then 5 μL of a solution of trypsin (1 mg mL^{-1}) was added to the diluted emulsions used for the PCS experiments. As the protein was broken up by the protease, the diameters of the emulsion droplets decreased and reached a steady value very shortly after the addition of trypsin; this diameter was again measured and the change in diameter was defined as equaling twice the thickness of the adsorbed layer of protein (Dalgleish, 1993). These trypsin-treated droplets were stable at least over 1 h, and no increases of diameter arising from aggregation were observed. It was established that the presence of Tween in the concentrations used did not affect the activity of the trypsin, because in all of the emulsions some changes in the diameter were observed when the trypsin was added.

Measurement of the ζ-Potential of the Emulsion Droplets. The ζ-potential of the droplets was measured using a Malvern Instruments Zetasizer 4. The measurement cell was set up and aligned so that the measurements were made in the stationary layer, where the electroosmotic effect is minimized. The emulsion, diluted 1:2000 in imidazole buffer, was introduced into the measurement cell and the electrophoretic mobility of the particles measured. Sets of 10 measurements were made on each sample, and the results were averaged. The ζ-potentials were calculated from the measured electrophoretic mobility by using the Smoluchowski approximation of Henry's equation (Darling and Dickson, 1979).

Determination of Surface Composition of Protein. The composition of protein adsorbed at the surface of the emulsion droplets was determined directly by analyzing the cream phase using SDS–PAGE under reducing conditions and photometric scanning of the stained protein bands, as described previously (Hunt and Dalgleish, 1994; Euston *et al.*, 1995).

RESULTS

The protein loads on the surfaces of emulsions prepared with all three protein concentrations, both in the presence and in the absence of Tween, were very similar to those which were measured, using a different homogenizing system, in previous experiments (Euston *et al.*, 1995). Essentially, when Tween was incorporated into the emulsion, the surface coverage of the proteins decreased almost linearly with the proportion of added surfactant. In agreement with earlier results on commercial caseinate, it was found that even 1% Tween was insufficient to displace all of the casein from the oil–water interfaces.

Surprisingly, and differing from previous observations (Fang and Dalgleish, 1993a), the thicknesses of the adsorbed layers around the emulsion droplets in the absence of Tween (as measured by the change in diameter during trypsin treatment) showed only small differences as the concentration of casein used to make the emulsions was altered (Figure 1). Previously, it had been found that 0.5% casein gave a substantially thinner adsorbed layer than 1.0 or 2.0% casein (Fang and Dalgleish, 1993a). However, repeated experiments in the present investigation confirmed that the layer thickness was not concentration-dependent. It was concluded that the preparation of caseinate used in these experiments (a commercially prepared spray-dried material) behaved differently from the one previously used (a freeze-dried laboratory preparation), although no definite reason can be given for this.

Studies of the dependence of the layer thickness on the surfactant concentration (Figure 1) showed that, as the concentration of Tween was increased, the hydrodynamic thickness of the adsorbed protein layer also

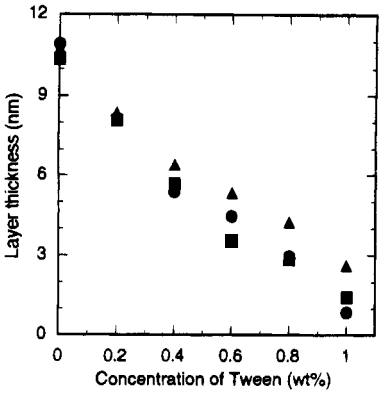

Figure 1. Thickness of the adsorbed layer of caseinate on the emulsion droplets, measured by PCS and trypsinolysis, in emulsions (20 wt % soy oil) containing different concentrations of caseinate and Tween 60. Points are shown for emulsions containing concentrations of caseinate of (■) 0.5%, (●) 1.0%, and (▲) 2%.

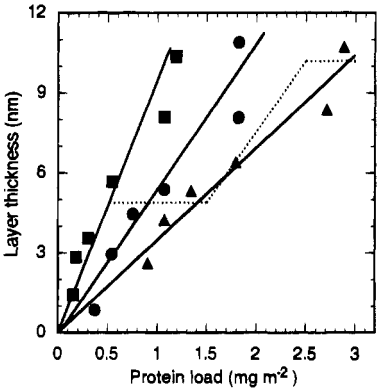

Figure 2. Thickness of the adsorbed layer of caseinate plotted against the protein load on the surfaces of the emulsion droplets. The protein load in each set was altered by increasing the amount of Tween present during emulsification. Points are shown for emulsions containing concentrations of caseinate of (■) 0.5%, (●) 1.0%, and (▲) 2%. The dotted line shows the thickness of adsorbed layers of casein in emulsions where the casein concentration is changed in the absence of other surfactant (Fang and Dalgleish, 1993a).

decreased. This may be explained by one of two mechanisms: either the layer is collapsed overall as protein is removed by the surfactant or the adsorbed protein molecules become spaced further apart and the adsorbed layer becomes more freely draining. Because Tween displaces casein, we expected the second of these mechanisms to be active (but see below).

Within the general trend of decreasing layer thickness (Figure 1) it could be seen that the effect of Tween was greatest on the emulsion containing 0.5% casein and least for the emulsion containing 2% casein, although the influence of overall protein concentration on the results was considerably less than for the small molecule surfactant; it was the concentration of Tween that mainly determined the behavior. When the changing layer thickness was plotted against the measured protein load (Γ) on the interface (Figure 2), it was immediately apparent that the points did not fall on the same curve for all of the casein concentrations; the effect of changing the protein load on the thickness of the adsorbed layer was greatest for the lower concentrations of protein. The plots of apparent layer thickness against Γ were approximately linear, in distinction to the behavior obtained when the surface coverage was changed simply by incorporating less protein into the emulsion when no Tween was present (Fang and Dalgleish, 1993a). In that situation, small amounts of adsorbed casein gave a thin layer and increasing the adsorbed concentration gave a step in the layer thickness (Figure 2, broken line), suggesting that casein adopted "extended" or "compact" conformations depending on the amount of casein available on the interface. In the present experiments, it was also clear that the thickness of the adsorbed layer did not simply depend on the protein load, but on other factors as well, because the results at different protein concentrations did not superimpose on one another.

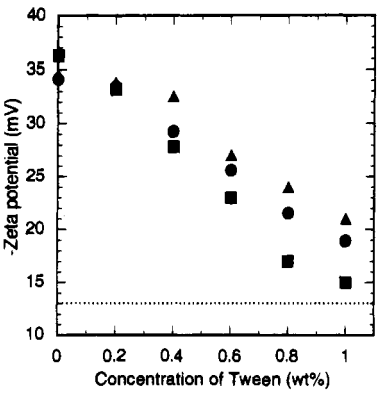

Figure 3. ζ-Potentials of the emulsion droplets in emulsions (20 wt % soy oil) containing different concentrations of caseinate and Tween 60. Points are shown for emulsions containing concentrations of caseinate of (■) 0.5%, (●) 1.0%, and (▲) 2%. The broken line shows the ζ-potential of droplets in an emulsion that was made using 1% Tween and oil but containing no protein.

The apparent ζ-potentials of the particles behaved in an almost analogous way to the thickness of the adsorbed layer. In the absence of Tween, all of the emulsions gave ζ-potentials in the region of -35 mV, and no significant difference was seen among them (Figure 3). For comparison, an emulsion made with Tween and oil, containing no caseinate, was found to have a ζ-potential of -13 mV. In the emulsions containing Tween and caseinate, the ζ-potential increased steadily, but slightly nonlinearly as the concentration of Tween was increased. Addition of 0.2% Tween had relatively little effect on the ζ-potential, but at higher concentrations the effect was proportionately greater. As with the diameters, the effect of incorporating Tween was most marked in the emulsions containing the lowest concentrations of protein. The effect of Tween in increasing the ζ-potential was greater than the effect of protein in decreasing it. As judged by ζ-potential, Tween did not completely displace the casein from any of the emulsions, even when it was in a large molar excess (90:1) over the protein, since the ζ-potentials of the emulsions containing protein were always greater than those of the emulsions containing Tween alone. This again is evidence for the resistance of the mixed casein system to displacement by surfactants. The results are similar, but not identical, to the results of Chen *et al.* (1995), who found that emulsions prepared using β-casein showed decreasing electrophoretic mobility when they were diluted into solutions containing increasing concentrations of Tween 20. However, in these experiments, the maximum Tween/protein ratio was much higher than we used (about 5000:1), and the results suggested that all of the casein was displaced by the small surfactant.

When the measured ζ-potentials were plotted against the protein load, it could be seen (Figure 4) that the ζ-potential was determined by factors other than simply

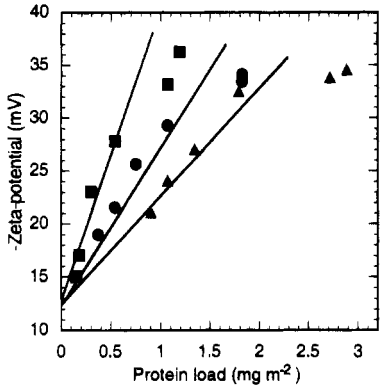

Figure 4. ζ-Potential of emulsion droplets plotted against the protein load on their surfaces. The protein load in each set was altered by increasing the amount of Tween present during emulsification. Points are shown for emulsions containing concentrations of caseinate of (■) 0.5%, (●) 1.0% and (▲) 2%. The point at zero protein load was measured in an emulsion that was made using 1% Tween and oil but containing no protein.

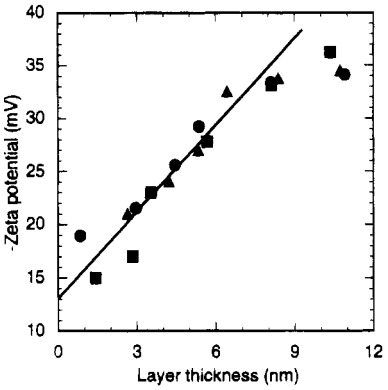

Figure 5. Correlation between the measured ζ-potential and the thickness of the adsorbed layer. Points are shown for emulsions containing concentrations of caseinate of (■) 0.5%, (●) 1.0%, and (▲) 2%. The points at highest ζ-potential and layer thickness are from the emulsions that contained no Tween.

the protein load on the surface of the emulsion droplets. Although the scatter of the points is higher than in Figure 2, it is again evident that the results for the three protein concentrations used do not coincide and that there is an approximately linear relationship between the ζ-potential and the protein load. All of the plots converge on the value for the ζ-potential of the emulsion made in the absence of protein. The points at highest protein load at all protein concentrations appear to fall off the lines linking the other points; this is a reflection of the nonlinearity of the results shown in Figure 3. Displacement of the first protein molecules has less effect than removal of the later ones.

DISCUSSION

The presence of Tween decreases the amount of protein adsorbed to the oil–water interface in the emulsions. Previous results of experiments involving β-casein and Tween show a nonlinear displacement of adsorbed protein by the Tween (Courthaudon *et al.*, 1991c), but in our experiments with commercial caseinate, the effect of small molecule surfactant in displacing protein is approximately linear with its concentration and behaves like a Langmuir system, where two components compete for the interface (Euston *et al.*, 1995). The differences between the two experiments are likely to reflect the different treatments that the two different protein preparations have undergone; one possibility is that the aggregation states of the caseins may differ, and it may be more difficult to displace aggregated casein than the unaggregated form.

The displacement of protein by Tween was of course measured in undiluted emulsions, and it has been assumed throughout that there was no change in the surface concentrations when the emulsions were diluted to make the light scattering measurements. This may be expected to be true for protein, which generally shows a high-affinity isotherm for adsorption, but may be less so for Tween, which might be expected to desorb when the concentration in solution is low. We cannot measure the surface concentrations in the diluted emulsion, but the lack of flocculation or coalescence of the emulsion droplets (which would necessarily result if the surfactants desorbed and left a bare interface) suggests that the Tween must remain on the surface even after dilution.

The effect of Tween on the hydrodynamics of the particles is seen both in the change in the apparent diameter and in the ζ-potential, since measurement of both of these properties depends on the measurement of the movement of the particles through the solution (i.e. Brownian or electrophoretic motion). This relationship between the two properties is clearly seen in Figure 5, where ζ-potential is plotted against apparent layer thickness. Over most of the range, a linear relationship obtains, with the only points lying off the line being those measured on emulsions containing no Tween and possibly those with 0.2% Tween. In this figure, it is apparent that there is no effect of protein concentration, because, no matter what is the structure of the interfacial layer, it affects both the measurement of thickness and ζ-potential equally. The change in the layer thickness arises because of the changing hydrodynamics of the particles, since the position of the surface of shear relative to the oil–water interface is altered as a result of the replacement of casein by Tween. Because the extended monolayer of casein (Fang and Dalgleish, 1993a) is replaced by a monolayer of small molecules, the particle becomes hydrodynamically smaller. This determines the apparent layer thickness and also affects the ζ-potential. However, there are other factors involved; as Tween replaces casein, the overall charge, and the charge density, is reduced; this, combined with the movement of the surface of shear, gives the altered ζ-potential.

The slopes of the lines in Figures 2 and 4 (i.e. the rate of change of thickness or of ζ-potential with protein load) gave a linear dependence when they were plotted against the reciprocal of the overall protein concentration (Figure 6). This shows that the layer thickness (t) is described by a relationship of the form

$$\mathrm{d}(t)/\mathrm{d}\Gamma = A + (B/[\mathrm{P}]) \quad (1)$$

and so

$$t = A\gamma + (B\gamma/[\mathrm{P}]) \quad (2)$$

where A and B are constants and [P] is the total concentration of protein. An analogous formulation will apply for the ζ-potential. If simply the surface properties were determined by the amount of adsorbed protein, then only the first term in the equation would suffice, i.e. t would be a function of Γ only (although not necessarily a linear one). Since Γ is in effect a measure of how closely the adsorbed protein molecules pack together, intuitively it would be expected that it would define the layer thickness. As we have seen, Γ is determined by the concentrations of both protein and Tween, the amount of oil, and the conditions of homog-

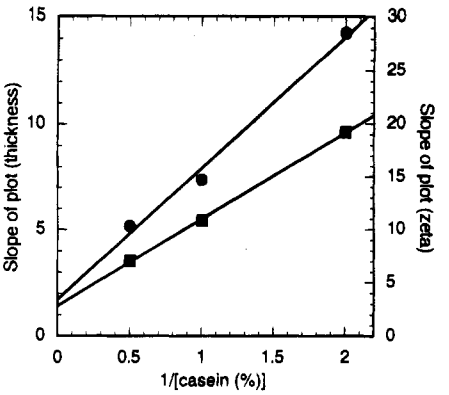

Figure 6. Slopes of the lines shown in Figures 2 and 4 plotted as functions of the reciprocal of the protein concentrations in the emulsions. Points ● refer to ζ-potential, and points ■ refer to the layer thickness.

enization; the last two are effectively constant in our experiments. The appearance of a second term in eq 2 shows that the structure of the adsorbed layer is not uniquely determined by the surface load of protein.

This is not true when the protein load is varied by changing the overall concentration of protein (Fang and Dalgleish, 1993a); in that case a step function is observed (Figure 2). Nor was a similar effect observed when mixtures of casein and phosphatidylcholine were used as surfactants in oil-in-water emulsions (Fang and Dalgleish, 1993b). In that case, the displacement of the casein was less, and the surfactant apparently adsorbed between casein molecules and allowed them to adopt a conformation that extended into solution; in effect, it made the layer thicker than normal at low Γ. With Tween, the effect appears to be more complex, since the thickness of the adsorbed layer is decreased compared with its original limiting value in the absence of Tween. The effect of this surfactant is to compress the casein layer rather than allow the molecules of protein to extend. Whether this is a conformational change brought about by interfacial spreading of the protein or by interaction between Tween and protein is conjectural, but it seems evident that the function of Tween in defining the properties of a casein-based emulsion is to control the conformation, as well as the concentration, of adsorbed protein at the droplet interfaces.

CONCLUSION

It is evident that the structures of the particles formed when casein is mixed with Tween as a surfactant in an oil-in-water emulsion are not simply determined by the amount of protein which is adsorbed to the interface and to the other surfactant "filling in" the gaps between protein molecules. Both the layer thickness and the ζ-potential of the adsorbed material change in such a way as to suggest that the structure of the adsorbed layer is determined by complex interactions between the protein, surfactant, and oil. Because of the presence of Tween, equilibria are likely to be established between protein in solution and in adsorbed states, so that the conditions during homogenization are likely to be less important than they are when only proteins are used as the surfactants. The results confirm that adsorbed casein is composed of flexible molecules, which may take up more or less space on an interface depending on the conditions.

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