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Hydrocolloids as emulsifiers and emulsion stabilizers☆

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ABSTRACT

We consider the essential molecular features of hydrocolloids having the ability to act as emulsifying agents and emulsion stabilizing agents. The criteria for effectiveness in protecting newly formed droplets against flocculation and coalescence are contrasted with the requirements to maintain long-term stability against aggregation, creaming and Ostwald ripening. To illustrate various aspects of stability behaviour, comparison is made between the physico-chemical characteristics of hydrocolloid emulsifying agents and those of other kinds of food emulsifying agents – surfactants, proteins and nanoparticles. Interfacial complexation between protein and polysaccharide may occur through covalent bonding or electrostatic bonding. For the case of electrostatic protein–polysaccharide complexes, the interfacial nanostructure and the stabilizing properties of the adsorbed layer are dependent, amongst other things, on the sequence of adsorption of the biopolymers to the emulsion droplet surface.

1. Introduction

One of the key functional roles of food hydrocolloids is in the preparation of emulsions and in the control of emulsion shelf-life. Product applications include carbonated soft drinks (Tan, 2004), ice-cream (Goff, 1997), and sauces and dressings (Sikora, Badrie, Deisingh, & Kowalski, 2008). Most hydrocolloids can act as stabilizers (stabilizing agents) of oil-in-water emulsions, but only a few can act as emulsifiers (emulsifying agents). The latter functionality requires substantial surface activity at the oil–water interface, and hence the ability to facilitate the formation and stabilization of fine droplets during and after emulsification (Dickinson, 2003, 2004).

The most widely used polysaccharide emulsifiers in food applications are gum arabic (*Acacia senegal*), modified starches, modified celluloses, some kinds of pectin, and some galactomannans (Dickinson, 2003; Garti & Reichman, 1993). The surface activity of these hydrocolloids has its molecular origin in either (i) the non-polar character of chemical groups attached to the hydrophilic polysaccharide backbone (in hydrophobically modified starch/cellulose) or (ii) the presence of a protein component linked covalently or physically to the polysaccharide (some gums, pectins, etc.). Protein ingredients derived from milk and eggs are the most commonly used food emulsifying agents; but these are not hydrocolloids (Dickinson, 1992). Due to its unique hydrophilic character, gelatin is really the only protein that can be properly categorized as a hydrocolloid. Gelatin does have some emulsifying ability, but its more characteristic roles are as a colloid stabilizer and gelling agent.

This article reviews ongoing research activity having the potential for providing new conceptual understanding about the optimum requirements for emulsification and stabilization by hydrocolloids and the basic mechanisms involved. One active area of current research is the stabilization of emulsions by conjugates and complexes of hydrocolloids with food proteins (Dickinson, 2008a). Another influence on emulsifier research in general is the renewed interest amongst physical scientists in emulsions (and foams) stabilized by finely dispersed particles (Aveyard, Binks, & Clint, 2003; Binks & Horozov, 2006; Hunter, Pugh, Franks, & Jameson, 2008; Leal-Calderon & Schmitt, 2008). Active research on nanoparticles and microparticles at interfaces is providing a stimulus for in-depth study of interfacial self-assembly of nanoparticles (Böker, He, Emrick, & Russell, 2007) and a systematic search for the optimum conditions promoting stabilization of droplets (and bubbles) by various kinds of emulsifying agents (Binks, 2003; Tcholakova, Denlov, & Lips, 2008). At the same time, natural protein-based nanoparticles – namely casein micelles – are being promoted as ideal encapsulation vehicles for neutraceuticals (Semo, Kesselman, Danino, & Livney, 2007). Against this background, the present review attempts to assess the benefits and implications of the trend towards biopolymer nanoparticles and biopolymer complexes as emulsifying and stabilizing ingredients.

We have to recognize, of course, that an important function of many hydrocolloid ingredients in oil-in-water emulsions is as a structuring/thickening/gelling agent in the aqueous medium. In

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conjunction with added 'weighting agents' to match the densities of oil and aqueous phases (Taherian, Fustier, Britten, & Ramaswarmy, 2008), the hydrocolloid is commonly perceived to slow down or even prevent creaming by modifying the rheology of the continuous phase. Xanthan gum is especially effective in this type of stabilizing role. This simple rheological control mechanism is most effective at low oil volume fractions, where individual droplets are separately immobilized in an entangled biopolymer network, and the small buoyancy force acting on each droplet is hardly sufficient to overcome the effective yield stress of the surrounding weak gel-like biopolymer matrix. Theoretically, a yield stress of just 10^{-2} Pa is sufficient to prevent the creaming of individual dispersed droplets in the size range below ~10 μm (Dickinson, 1988).

For concentrated emulsions containing a significant amount of free hydrocolloid in the aqueous phase, an alternative explanation based on polymer-induced depletion forces is now regarded as more appropriate (Moschakis, Murray, & Dickinson, 2005, 2006; Parker, Gunning, Ng, & Robins, 1995). At very low concentrations, the added hydrocolloid has a destabilizing effect on the emulsion, since the depletion flocculation induced by the non-adsorbing hydrocolloid causes enhanced serum separation of the emulsion. But at higher added hydrocolloid concentrations (still <0.1 wt% for the case of xanthan gum), when the depletion interactions are stronger, creaming is inhibited due to the viscoelastic character of the interconnected regions of emulsion droplets that have become flocculated into a gel-like network. The system becomes kinetically trapped on the microscopic scale in a phase-separated state. For an emulsion containing <0.1 wt% xanthan, the local viscosity of the oil-droplet-rich regions has been estimated to be as much as 10^3 times larger than that for the neighbouring xanthan-rich regions (Moschakis et al., 2006). Moreover, the oil-droplet-rich microphase viscosity has been found to increase dramatically with xanthan concentration. So, although the xanthan-containing phase does become more viscoelastic with more xanthan present in the system, the main influence of the added hydrocolloid stabilizer on the overall rheology of the emulsion is through its effect on the oil droplet network. In the presence of added hydrocolloid, the kinetics of phase separation (leading in the long-term to enhanced gravity creaming and macroscopic serum separation) is controlled in the short/medium term by the rheological behaviour of the interconnected oil droplet regions. That is, the gravitationally unstable liquid-like emulsion has become transformed into a stable gel-like emulsion containing trapped 'blobs' of hydrocolloid-structured water (Dickinson, 2006a).

2. Physico-chemical processes involved in the making of emulsions

To form a fine emulsion, large deformable drops must be broken down by the vigorous application of mechanical energy (Dickinson, 1994; Walstra, 1983; Walstra & Smulders, 1997). In food processing this can be traditionally achieved using a high-speed mixer, a colloid mill, or a high-pressure valve homogenizer. Thermodynamically speaking, the process is extremely inefficient, with most of the power being dissipated as heat.

Emulsification involves the sudden creation of a large amount of new liquid interface. Thermodynamics tells us that, in order to increase the oil–water surface area by an amount ΔA, the required work (free energy change) is $\Delta G = \gamma \Delta A$, where γ is the interfacial tension. Let us suppose that we wish to make an oil-in-water emulsion of 10 vol% oil containing uniform droplets of radius 1 μm using an emulsifier which reduces the interfacial tension to $\gamma \sim 5\ \mathrm{mN\,m^{-1}}$. From thermodynamics, we can estimate that the theoretical work associated with making the new interface is $\Delta G \sim 10^3\ \mathrm{J\,m^{-3}}$. But in practice the actual amount of work required to make such an emulsion is of the order of $10^6\ \mathrm{J\,m^{-3}}$, i.e., a thousand times larger! The reason for this gross discrepancy is that small droplets have highly curved interfaces, and the breaking of larger droplets into smaller ones requires the rapid application of a disruptive force to overcome the interfacial forces holding the larger droplet together. To disrupt a droplet of radius a requires an external pressure gradient of magnitude $\Delta p/a = 2\gamma/a^2$, where Δp is the Laplace pressure. This implies a pressure gradient of the order of $10^{10}\ \mathrm{Pa\,m^{-1}}$ (i.e. 1 kbar $\mathrm{cm^{-1}}$). During homogenization, the fluctuating stress differences needed to produce such a high local pressure gradient are generated from the intense laminar flow (shear and extensional deformations) and/or inertial effects (turbulence and cavitation) (Dickinson, 1994; Walstra, 1983).

The main role of the emulsifier is to adsorb at the surface of the freshly formed fine droplets and so prevent them from coalescing with their neighbours to form larger droplets again (see Fig. 1). For a fixed rate of energy dissipation during emulsification, the final droplet-size distribution is determined by the time taken for the interface to be covered with emulsifier, as compared with the average time interval between droplet collisions. When the

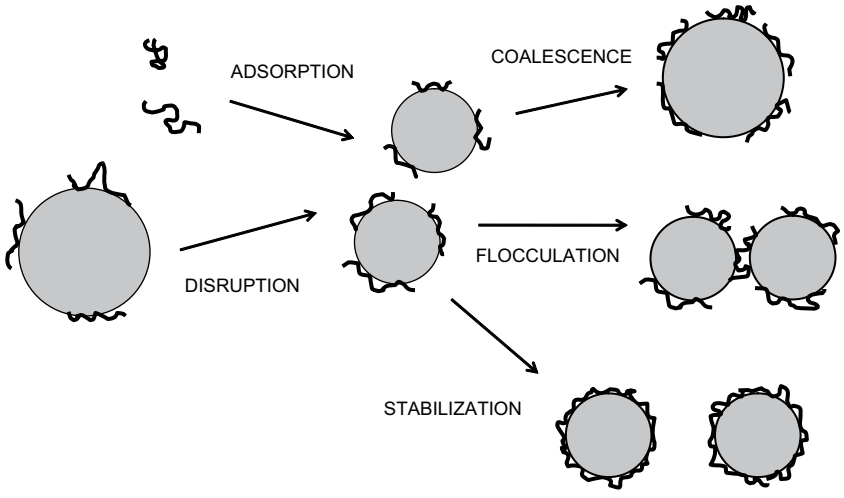

Fig. 1. Illustration of main physico-chemical processes involved in making of emulsions. Stabilization of fine droplets requires mechanical disruption of coarse droplets accompanied by rapid effective adsorption of emulsifier at the new oil–water interface. Collision of droplets with insufficient coverage of emulsifier leads to coalescence and/or flocculation.

emulsifier adsorbs too slowly, or is present at too low a concentration, most of the individual droplets formed during the intense energy dissipation of emulsification are not retained in the final emulsion. This may be due to breakage of the thin film between colliding droplets (coalescence) or sharing of the adsorbed layer between two droplets (bridging flocculation). The latter phenomenon is prevalent in concentrated emulsions (e.g., homogenized cream) which have a relatively low emulsifier/oil ratio, and in less concentrated systems containing mixed polymeric emulsifiers of different surface activity (Dickinson & Galazka, 1991a). For systems of high emulsifier/oil ratio being homogenized in efficient equipment, the droplets produced are non-flocculated and polydisperse, and the mean droplet size is not so dependent on the emulsifier concentration, but rather is mainly controlled by the hydrodynamic processes of droplet disruption (Jafari, Assadpoor, He, & Bhandari, 2008; Taisne, Walstra, & Cabane, 1996).

Under the turbulent flow conditions of high-pressure homogenization, the transport to the interface is dominated by convection. This is different from diffusion under quiescent conditions which determines the mass transport during the laboratory measurement of time-dependent interfacial tension. In diffusive mass transport, the most rapidly adsorbing species are low-molecular-weight surfactants and individual protein molecules, because these have relatively high diffusion coefficients. In convective mass transport, however, the most rapidly adsorbing species are colloidal particles (e.g., casein micelles) and large macromolecules (e.g., hydrophobically modified starch) (Nilsson & Bergenståhl, 2007a; Nilsson et al., 2007). With particulate and aggregated macromolecular species adsorbing to the oil–water interface, the amount of emulsifying agent required to saturate the surface can be much higher than for small-molecule emulsifiers or soluble proteins.

An effective emulsifier is therefore one that (i) rapidly reduces the interfacial tension at the freshly formed oil–water interface, (ii) binds strongly to the interface once adsorbed, and (iii) protects the newly formed droplets against flocculation or coalescence. This protection against immediate recoalescence occurs in the first place *via* dynamic surface tension effects (the Gibbs–Marangoni mechanism) and later *via* repulsive colloidal interactions (electrostatic and steric stabilization mechanisms) (Dickinson, 1992). With polymeric emulsifiers at relatively low concentrations, the kinetics of emulsifier adsorption is commonly the rate-determining factor. In many food situations, the kinetics of adsorption and the processes of interface stabilization are complicated by the fact that the emulsifying species are polydisperse in size and in chemical composition. During emulsification with protein as the main emulsifier, the presence of even a small quantity of rapidly adsorbing surfactant can facilitate substantial reduction in the mean droplet size (Courthaudon, Dickinson, & Dalgleish, 1991). A rather higher concentration of a miscible cosolute (e.g., 10–20% ethanol), whose presence lowers the surface tension of the aqueous phase, can play a similar role (Burgaud & Dickinson, 1991). Due to the Gibbs–Marangoni mechanism, not all the fresh oil–water interface has to be fully saturated with emulsifier for the individual droplets to be protected against recoalescence (Dickinson, 1994). It should be noted, however, that the Gibbs–Marangoni effect only operates if the emulsifying agent is present in the continuous phase (Bancroft's rule).

3. Relative effectiveness of various hydrocolloid emulsifying agents

It is generally important that emulsion droplets are made as small as possible in order to minimize gravity creaming effects (Dickinson, 1988). A convenient way to evaluate the relative effectiveness of an emulsifier under controlled hydrodynamic conditions is to determine the bulk emulsifier concentration required to produce the minimum mean droplet size (maximum surface area per unit volume of oil). Fig. 2A shows data for triglyceride oil-in-water emulsions (15 wt% oil, pH = 3.0) taken from the recent careful study of Nakauma et al. (2008). The surface–volume mean diameter $d_{3,2}$ is plotted against emulsifier concentration for three different hydrocolloids: gum arabic (GA), soybean soluble polysaccharide (SSPS), and sugar beet pectin (SBP). It was reported (Nakauma et al., 2008) that the $d_{3,2}$ values remained constant and essentially independent of hydrocolloid concentration above 1.5%, 4% and 10% for SBP (0.55 μm), SSPS (0.66 μm) and GA (0.82 μm), respectively. Hence, the relative abilities of these hydrocolloids as emulsifying agents at pH = 3 were found to lie in the order SBP > SSPS > GA.

In deciding whether to choose a hydrocolloid or a protein ingredient as the primary emulsifying agent in any food application, the manufacturer must consider the nature of the environmental conditions to which the system will be subjected. These conditions include factors such as temperature, pH, ionic strength, calcium ion content, and so on. When conditions are favourable, protein emulsifiers tend to be more efficient. Proteins have greater

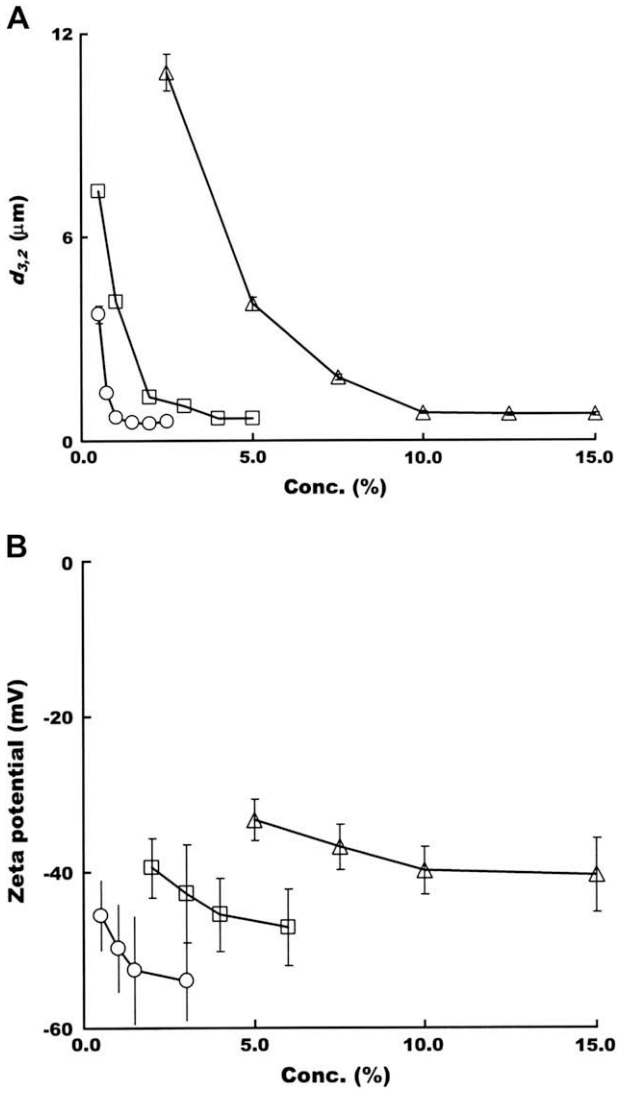

Fig. 2. Comparison of properties of freshly made emulsions (15 wt% triglyceride oil, pH = 3.0) prepared under controlled hydrodynamic conditions with three different food hydrocolloids: △, gum arabic; □, soybean soluble polysaccharide; ○, sugar beet pectin. Plotted against the hydrocolloid emulsifier concentration are (A) mean droplet diameter $d_{3,2}$ and (B) zeta potential. (With permission from Nakauma et al., 2008.)

binding affinities and surface activities than polysaccharide-based emulsifiers, and they have lower saturation surface loads (1–2 mg m^{-2}). These factors mean that, compared with a hydrocolloid, a much lower concentration of protein emulsifier (sodium caseinate, β-lactoglobulin, etc.) can be used to stabilized a fine oil-in-water emulsion (Dickinson, 2001). The performance problem of protein-stabilized emulsions, however, relates to the major contribution of electrostatic interactions to the adsorbed layer structure. Combined with the low surface coverage, this makes the emulsions susceptible to destabilization under unfavourable environmental conditions. For instance, casein-based protein emulsions are highly sensitive to destabilization by acidification and calcium ions (Dickinson, 2006b), and whey protein-based emulsions are rather heat-sensitive (Dickinson & Parkinson, 2004). In contrast, the large molecular size and predominant hydrophilicity of a polysaccharide emulsifier allows for the formation of a thicker stabilizing layer that is capable of protecting droplets against aggregation over a wide range of unfavourable conditions, such as thermal shock treatment and the addition of calcium salts (Chanamai & McClements, 2002).

Starch that has been hydrophobically modified by reaction with octenyl succinate anhydride has been shown to be strongly surface-active (Prochaska, Kedziora, Le Thanh, & Lewandowicz, 2007) and to have excellent emulsifying and emulsion stabilizing properties (Chanamai & McClements, 2002; Nilsson & Bergenståhl, 2007a; Taherian, Fustier, & Ramaswamy, 2007). The short octenyl succinate side chains anchor the carbohydrate polymers to the oil–water interface, and the long amylopectin backbone protects the droplets against flocculation by the mechanism of steric stabilization (Dickinson, 1992). Good stabilization by adsorbed polysaccharides can also be achieved with various surface-active derivatives of cellulose such as hydroxypropyl (methyl)cellulose (Wollenweber, Makievski, Miller, & Daniels, 2000). Like hydrophobically modified starch, these macromolecules form viscous adsorbed layers at liquid–liquid interfaces, and their dynamic adsorption behaviour and surface rheological properties have been the subject of recent investigations (Erni et al., 2007; Mezdour, Cuvelier, Cash, & Michon, 2007; Perez, Carrera Sanchez, Pilosof, & Rodriguez Patino, 2008). Despite this extensive research activity, however, there has been no definitive demonstration that the surface rheology of a hydrocolloid is directly correlated with its emulsification (or foaming) behaviour.

Some studies of the interfacial properties of chemically modified polysaccharides have been motivated by a commercial drive to develop replacements for gum arabic in the emulsification of flavour oils for soft drinks. The emulsifying properties of gum arabic are associated with a high-molecular-weight fraction representing less than 30% of the total hydrocolloid (Randall, Phillips, & Williams, 1988; Ray, Bird, Iacobucci, & Clark, 1995). The protein is covalently bound to the carbohydrate in the form of a mixture of arabinogalactan–protein complexes, each containing several highly branched polysaccharide units linked to a common protein core. The protein chain firmly anchors the complex to the oil–water interface, and the charged polysaccharide units attached to the protein chain provide a steric barrier against droplet flocculation. Gum arabic is an extremely effective emulsifier at low pH, at high ionic strength, and in the presence of beverage colouring agents. But the gum is expensive to use in practice because a rather high gum/oil ratio ($\sim$1:1) is required in order to produce fine stable emulsion droplets ($d_{32} << 1$ μm) (McNamee, O'Riordan, & O'Sullivan, 1998; Nakauma et al., 2008). As well as chemically modified starch/cellulose, several replacements for gum arabic have been proposed: certain kinds of pectin (Akhtar, Dickinson, Mazoyer, & Langendorff, 2002; Siew & Williams, 2008; Williams et al., 2005), other natural gums (Garti, 1999; Yadav, Johnston, Hotchkiss, & Hicks, 2007; Yadav, Parris, Johnston, & Hicks, 2008), and protein–polysaccharide conjugates (Akhtar & Dickinson, 2007; Dickinson, 2008b).

In experimental studies of emulsifier effectiveness, a commonly reported property is the zeta potential (ζ) of the emulsion droplets. Fig. 2B shows some reported values of ζ at pH = 3.0 from the work of Nakauma et al. (2008) for the same three hydrocolloids (SBP, SSPS and GA) as considered in Fig. 2A. According to the conventional wisdom, the larger the absolute magnitude of ζ, the greater is the electrostatic repulsion between droplets, and therefore the better the stability. Thus, from the data in Fig. 2B, sugar beet pectin (SBP) should produce the most stable emulsion. But, in reality, the opposite has been found to be the case (Nakauma et al., 2008): as measured by the change in $d_{3,2}$ on storage, emulsions made with SBP exhibited the poorest stability. This unreliability of the zeta potential as a indicator of relative emulsion stability arises in part because the classical double-layer theory used to estimate ζ from electrophoretic mobility measurements assumes a solid charged particle which moves relative to the electrolyte dispersion medium at a well-defined plane of shear (Dickinson, 1992). For a polyelectrolyte-coated surface, the plane of shear is ill-defined because it is dependent on the unknown hydrodynamic flow of solvent within the polymer layer, which in turn is related to the generally unknown distribution of polymer, solvent and ions within the layer. Hence, it cannot be correct to treat hydrocolloid-coated emulsion droplets as if they are simple charged spheres. More significantly, though, what the experimental observations of ζ clearly demonstrate is the overriding importance of steric repulsion to the stabilizing properties of a hydrocolloid emulsifying agent like gum arabic or modified starch.

4. Hydrocolloids versus proteins, surfactants and (nano)particles

Hydrocolloid emulsifiers have certain general functional characteristics resembling those of all the other main categories of food emulsifying agents: proteins, surfactants and solid particles. Nevertheless, being hydrophilic polymer molecules, hydrocolloids also differ in certain respects from these other species. As an aid to understanding the structure/function relationship of hydrocolloids, we here compare these ingredients in more detail.

When the emulsifier concentration is low, and electrostatic interactions are largely suppressed, the emulsification behaviour is qualitatively similar for all the various types of emulsifiers. That is, the initially formed droplets are only partially covered with polymer/protein/surfactant/particles, and the droplets coalesce with others until their surfaces become protected by a dense layer of molecules/particles. Additionally, bridging flocculation may occur due to sharing of droplet surfaces by adsorbed particles or macromolecules (see Fig. 1). When the emulsifier concentration is high, though, the mean droplet size depends on the emulsifier type exclusively through the interfacial tension. The relevant property here is the equilibrium (static) tension for fast adsorbing surfactants, but it is the dynamic surface tension for the more slowly adsorbing macromolecular emulsifiers, i.e., proteins and, especially, hydrocolloids. For particle emulsifiers acting alone, the relevant property is the interfacial tension of the bare oil–water interface (Tcholakova, Denkov, & Lips, 2008).

Once an emulsion has been formed, the main factor determining stability is the strength/range of the repulsive interactions between pairs of closely approaching droplet surfaces (Dickinson, 1992; McClements, 2005). Except at very low ionic strength, when long-ranged electrostatic repulsion is important, the minimum interdroplet separation is mainly determined by the physical space occupied by the species present in the adsorbed monolayer. Fig. 3 illustrates that, for these different kinds of emulsifying agents, the relative thickness of thin films between pairs of closely approaching droplet surfaces will tend to lie in the order: surfactants < proteins < hydrocolloids < particles.

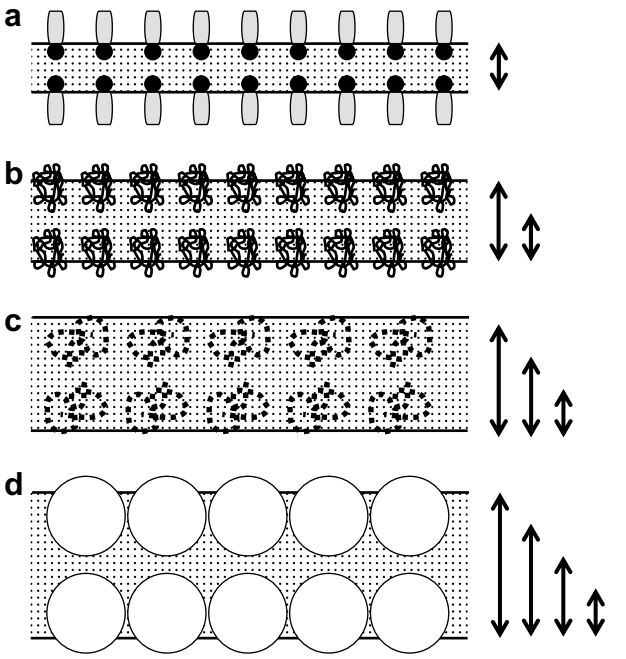

Fig. 3. Schematic representation of relative thicknesses of thin films between closely approaching oil droplets stabilized by (a) surfactants, (b) proteins, (c) hydrocolloids and (d) colloidal particles. The diagrams illustrate effects of differences in sizes of the different kinds of adsorbed species, i.e., surfactant molecules (0.5–1 nm), proteins (1–5 nm), hydrocolloids (5–10 nm), and particles (10 nm to several μm).

Particles adsorbed at the surface of liquid droplets provide an obvious mechanical barrier against flocculation and coalescence. The protective barrier is more effective when the particles lie predominantly on the convex side of the oil–water interface, i.e., they are preferentially wetted by the continuous phase. A particle's position with respect to the interface is determined by the contact angle θ. Fig. 4 illustrates the case of a spherical particle wetted preferentially by water ($\theta < 90°$). The free energy of spontaneous desorption (ΔG_d) is proportional to $[r(1-\cos\theta)]^2$, where r is the particle radius (Dickinson, 2006c). Therefore, as long as the contact angle is not very close to 0° (or 180°), the magnitude of ΔG_d for an adsorbed particle of colloidal size is extremely high compared with the thermal energy (kT), and so the particle can be regarded as irreversibly adsorbed. Even a relatively small nanoparticle – down

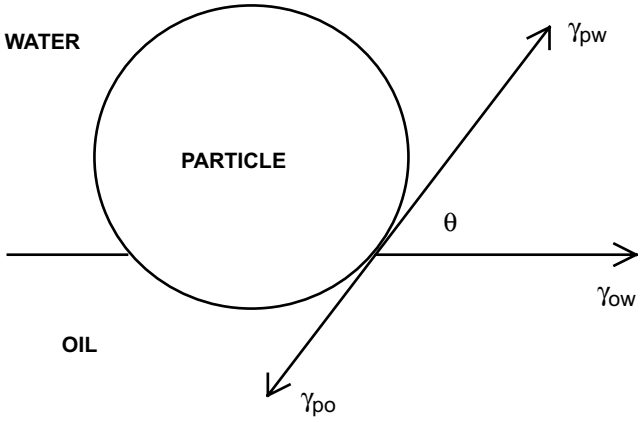

Fig. 4. Sketch of the location of a single spherical particle at the oil–water interface. The contact angle θ is the angle formed at the junction point of particle (p), oil (o) and water (w). The tensions at the three separate interfaces are γ_{po}, γ_{pw} and γ_{ow}, and the angle is defined by $\cos\theta = (\gamma_{po} - \gamma_{pw})/\gamma_{ow}$ (Young's equation).

to the size of a large protein molecule (say, 5–10 nm) – can be regarded as being essentially irreversibly adsorbed, so long as the contact angle is not too low (Dickinson, 2006c).

This concept of irreversible adsorption of solid (nano)particles at the oil–water interface has led to the belief that oil droplets possessing a full monolayer coverage of particles can be regarded as having essentially indefinite stability. An alternative arrangement to this two-layer stabilization (Fig. 3d) would be stabilization by a single layer of bridging particles, where the major portion of each particle lies in the aqueous continuous phase (Lopetinsky, Masliyah, & Xu, 2006). This type of bridging aggregation without coalescence is also possible with some protein emulsifiers – but definitely not with surfactants, and generally not with hydrocolloids. With particle emulsifiers in either the bilayer or the single-layer configurations, steric hindrance prevents particle displacement from the interface as well as lateral displacement within the interface. Another mechanism contributing towards the prevention of coalescence is the stability of the thin film of continuous phase between particle-coated droplets, as influenced by the capillary pressure in the film and the surface rheological properties (Lopetinsky et al., 2006). Despite these theoretical considerations, however, the limited experimental evidence available (Tcholakova et al., 2008) does not support the hypothesis that particle-stabilized emulsions are more stable with respect to droplet–droplet coalescence, as compared with typical surfactant-stabilized or protein-stabilized emulsions. This same conclusion would also appear to be applicable to a comparison of (nano)particles and hydrocolloids as protectors against coalescence.

Another phenomenon contributing to emulsion instability is Ostwald ripening. This involves smaller droplets (<1 μm) shrinking and disappearing at the expense of the growth of bigger droplets (>1 μm). The thermodynamic driving force for this process is the difference in chemical potentials of molecules in the smaller and larger droplets (Dickinson, 1992). Mass transport takes place by diffusion between droplets. Thus, for Ostwald ripening to occur at a significant rate, the dispersed phase must have appreciable solubility in the continuous phase. (Because gases are highly soluble in water, the mechanism is especially important for aqueous foams.) Hence, the process is significant for beverage emulsions containing water-soluble flavour oils (D-limonene, etc.), whereas it is insignificant for dairy-type emulsions containing water-insoluble triglyceride oils. For a water-soluble soluble oil, the most effect way to resist the ripening process is to mix it with an insoluble oil (e.g., vegetable oil + citrus oil in a cloudy beverage emulsion formulation).

Depending on the type of emulsifier, there are important differences in the Ostwald ripening behaviour (Tcholakova et al., 2008). With low-molecular-weight surfactants, the interfacial tension is low, which reduces the thermodynamic driving force. And because surfactant adsorption is reversible, the tension remains essentially constant as the emulsifier is continuously desorbed during droplet shrinkage (see Fig. 5a). The presence of micelles in the aqueous phase enhances further the effective solubility of the dispersed phase, which increases the mass transport rate.

With a typical globular protein as emulsifier, droplet shrinkage leads to a greater surface coverage and a thicker layer, since the emulsifier resists desorption. The consequent lowering of the tension, associated with the high viscoelasticity of the adsorbed layer, leads to a slowing down of the ripening process. But the ripening rate of the emulsion can be stopped completely in only two ways: (a) if there are insoluble species present in the oil phase (like vegetable oil added to an essential oil in a cloudy beverage emulsion), or if the (elastic) protein layer reaches a thickness similar to the droplet radius (Meinders & van Vliet, 2004). Over

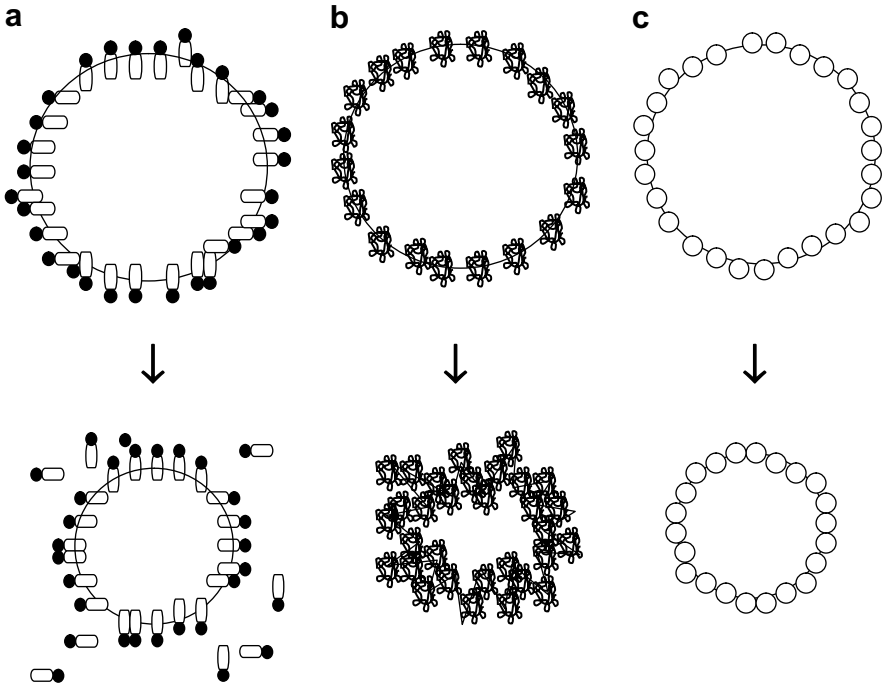

Fig. 5. Schematic representation of the effect of emulsifier type on the shrinkage behaviour of a small emulsion droplet as a consequence of Ostwald ripening: (a) surfactant-stabilized, (b) protein-stabilized, and (c) particle-stabilized.

extended time-scales, a monolayer protein film is predominantly viscous, which means that there is no complete arrest of the ripening process: compression to high surface pressures leads to slow protein desorption, and local interfacial stresses around small droplets causes wrinkling of the residual protein film (see Fig. 5b). (In the case of a shrinking (globular) protein-stabilized gas bubble, there is complete loss of the dispersed phase, leaving just a residual protein aggregate – Dickinson, Ettelaie, Murray, & Du, 2002.) When the emulsifier is sodium casein(ate), which contains disordered amphiphilic protein molecules, the mechanistic behaviour can be considered as intermediate between the surfactant case and the globular protein case.

Due to the exceptionally high desorption energy, particulate emulsifiers are able to prevent Ostwald ripening completely (Binks, 2003; Cervantes Martinez et al., 2008). The reduction in surface area on droplet shrinkage produces a tightly jammed particle monolayer (see Fig. 5c). This leads to an inward bending of the oil–water interface between the particles. The creation of micro-configurations having zero mean curvature of fluid interface between the particles (i.e., a vanishing apparent interfacial tension) eliminates the capillary pressure that drives the ripening process (Tcholakova et al., 2008). Any hydrocolloid emulsifier that could behave like a rigid spherical nanoparticle at the oil–water interface could also produce a tightly jammed stabilizing monolayer. But most hydrocolloids have 'soft' polymer-like structural characteristics, more resembling proteins than solid particles; hence they cannot fully arrest Ostwald ripening.

5. Interactions of hydrocolloids with adsorbed proteins

There is increasing interest in exploiting the combined advantages of proteins and hydrocolloids as functional ingredients *via* the development of protein–polysaccharide complexes as emulsifiers and stabilizers (Dickinson, 1995, 2008a, 2008b; Guzey & McClements, 2006). The protein and polysaccharide components may be joined together by either (i) covalent bonding or (ii) electrostatic interactions.

Covalent linkage of protein to polysaccharide can be achieved in various ways. Direct chemical means can be used to form gelatin–pectin hybrids linked by amide bonds by incubating a mixture of gelatin (type A) + high-methoxyl pectin under alkaline conditions (Diftis, Pirzas, & Kiosseoglou, 2005). Alternatively, conjugation may be achieved enzymatically, e.g., using peroxidase to attach β-casein to feruloylated arabinoxylan (Boeriu *et al.*, 2004) or transglutaminase to attach sodium caseinate to gum arabic (Flanagan & Singh, 2006). But probably the most convenient method of conjugation is simply to heat an intimate dry mixture of the protein + polysaccharide (Dickinson & Galazka, 1991b; Kato, Sasaki, Furuta, & Kobayashi, 1990; Oliver, Melton, & Stanley, 2006). This dry-heat-induced conjugation invariably improves protein solubility and stability under unfavourable solution conditions of low pH and high ionic strength, with consequent benefits for protein emulsification properties (Oliver et al., 2006; Dickinson, 2008a). The growing acceptance of these Maillard-type conjugates as potentially valuable functional ingredients in various food applications is indicated by the broad range of protein + polysaccharide combinations that have been recently investigated (see Table 1).

Due to the bound protein, the conjugate is much more surface-active than the polysaccharide on its own; hence the conjugate is able to achieve surface layer saturation at a much lower bulk concentration. At the same time, due to the covalently bound polysaccharide, the adsorbed protein layer is protected against destabilization under unfavourable environmental conditions (e.g., heating, low pH, high electrolyte concentrations, etc.). The large size and hydrophilicity of the polysaccharide moiety generates long-range steric repulsion between emulsion droplets surfaces. Theoretical calculations have recently shown (Ettelaie, Akinshina, & Dickinson, in press) that a strong association of a specific part of a moderately large polysaccharide entity (>5–10 kDa) to an adsorbing protein can confer sufficient additional steric stabilization to overcome any surface–surface attractive interaction that might be present with the adsorbed protein alone under unfavourable conditions of pH and/or ionic strength. While this interfacial biopolymer structure is most efficiently realised with

Table 1
Experimental studies of the characterization and functionality of Maillard-type protein–polysaccharide conjugates published during 2004–2007

Protein	Polysaccharide	Reference(s)
β-Casein	Dextran	Mu, Pan, Yao, & Jiang, 2006
β-Lactoglobulin	Chitosan	Miralles, Martinez-Rodriguez, Santiago, van de Lagemaat, & Heras, 2007
β-Lactoglobulin	Dextran	Dunlap & Côté, 2005; Jimenez-Castaño, Villamiel, & Lopez-Fandiño, 2007; Jimenez-Castaño, Villamiel, Martin-Alvarez, Olano, & Lopez-Fandiño, 2005; Wooster & Augustin, 2006
β-Lactoglobulin	Gum arabic	Schmitt, Bovay, & Frossard, 2005
Ovalbumin	Dextran	Choi, Kim, Park, & Moon, 2005
Sodium caseinate	Dextran	Fechner, Knoth, Scherze, & Muschiolik, 2007
Sodium caseinate	Maltodextrin	Morris, Sims, Robertson, & Furneaux, 2004
Sodium caseinate	Pectin	Einhorn-Stoll, Ulbrich, Sever, & Kunzek, 2005
Soybean protein	Dextran	Diftis, Biliaderis, & Kiosseoglou, 2005
Soybean protein	Porphyran	Takano, Hattori, Yoshida, Kanuma, & Takahashi, 2007
Soy protein hydrolysate	Curdlan	Fan et al., 2006
Whey protein	Carboxymethyl cellulose	Kita, Korlos, & Kiosseoglou, 2007
Whey protein	Dextran	Wooster & Augustin, 2007
Whey protein	Maltodextrin	Akhtar & Dickinson, 2007
Whey protein	Pectin	Einhorn-Stoll et al., 2005; Nierynck, van der Meeren, Bayarri Gorbe, Dierckx, & Dewettinck, 2004

a permanent covalent linkage, a more common situation in food emulsion systems is where protein–polysaccharide complexation arises from non-covalent association driven by electrostatic interactions (Dickinson, 1998).

Two of the most traditional food ingredients are casein and gelatin. While both these ingredients consist of macromolecules that are disordered, polydisperse and heterogeneous, the two kinds of biopolymers differ substantially in terms of hydrophilic/hydrophobic balance, surface activity and intermolecular interactions. Furthermore, at neutral pH in the absence of calcium ions, whereas sodium caseinate forms low-viscosity mobile adsorbed layers at the oil–water interface, gelatin forms time-dependent gel-like stabilizing layers at the surface of emulsion droplets. This contrasting behaviour has been demonstrated (Dickinson, Murray, & Stainsby, 1985) in interfacial experiments on systems containing a binary mixture of the two proteins. Fig. 6 shows the observed change in surface shear viscosity on injecting sodium caseinate below a previously adsorbed gelatin layer at the planar hydrocarbon–water interface (Dickinson, Murray, Murray, & Stainsby, 1987). While the surface viscosity was at first greatly diminished, it subsequently recovered to values similar to those of the original aged gelatin film. The longer the film had been aged prior to addition of caseinate, the more rapid was the recovery. This behaviour can be interpreted in terms of the competitive displacement of the original primary adsorbed layer of gelatin by the more surface-active caseinate, followed by restructuring of the displaced hydrocolloid as a secondary gel-like layer below the new primary caseinate layer (as shown diagrammatically in the insets to Fig. 6). Though gelatin is unique in exhibiting thermoreversible self-association behaviour through triple-helix hydrogen bonding interactions, a qualitatively similar kind of protein–hydrocolloid organization at the oil–water interface can be expected with many other systems possessing favourable associative biopolymer–biopolymer interactions.

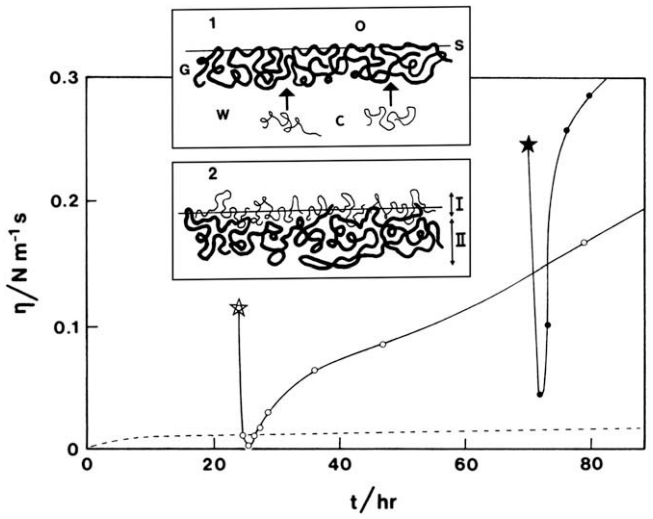

Fig. 6. Influence of sodium caseinate on the time-dependent surface shear viscosity $\eta(t)$ of gelatin at the *n*-hexadecane–water interface (pH = 7, 25 °C). The film adsorbed from a 10^{-3} wt% gelatin solution had been aged for 24 h (☆) or 72 h (★) prior to introducing 10^{-3} wt% caseinate into the aqueous sub-phase. The dashed line denotes $\eta(t)$ for 10^{-3} wt% caseinate in the absence of gelatin. Inset pictures 1 and 2 show schematic representations of the structure in the vicinity of the O/W surface (S) before and after penetration of casein molecules (C) into the adsorbed layer of gelatin molecules (G). In the postulated structure after caseinate addition, region I mainly determines the surface pressure and region II dominates the surface rheology. (Taken from Dickinson et al., 1987.)

For use as particulate structuring agents in food colloids, it would seem that there is considerable potential for the exploitation of electrostatic protein–polysaccharide complexation in the formulation of stable biopolymer-based nanoparticles by simple mixing, e.g., whey protein + gum arabic (Weinbreck, de Vries, Schrooyen, & de Kruif, 2003) or sodium caseinate + gum arabic (Ye, Flanagan, & Singh, 2006). Also novel protein–polysaccharide aggregates may be formed using static high-pressure technology to dissociate and reassemble of native casein micelle particles in the presence of interacting hydrocolloids such as low-methoxyl pectin or ι-carrageenan (Abbasi & Dickinson, 2002, 2004).

In model emulsion studies, there have been numerous cases reported in the recent literature in which the rheological and stability properties can be attributable to the presence of associative interfacial interactions between protein and polysaccharide ingredients. Some recent examples include systems containing whey protein + carboxymethylcellulose (Girard, Turgeon, & Paquin, 2002), sodium caseinate + low-methyoxl pectin (Matia-Merino & Dickinson, 2004), sodium caseinate + high-methoxyl pectin (Bonnet, Corredig, & Alexander, 2005), β-lactoglobulin + high-methoxyl pectin (Guzey, Kim, & McClements, 2004), canola protein + κ-carrageenan (Uruakpa & Arntfield, 2005), whey protein + xanthan gum (Benichou, Aserin, Lutz, & Garti, 2007), and sodium caseinate + gellan gum (Sosa-Herrera, Berli, & Martinez-Padilla, 2008).

Together with other factors like pH and ionic strength, the mesoscopic structure of the composite interfacial layer containing both protein and polysaccharide has been recognized to be dependent on the procedure used to make the emulsion (Dickinson, 2008b). Two alternative procedures are differentiated in Fig. 7. Method (a) is to prepare a mixed solution of the biopolymers, and then use the resulting protein–polysaccharide complex as the emulsifying agent during homogenization. Method (b) is to make the emulsion initially with protein as emulsifying agent, mix the washed emulsion with polysaccharide solution, and then allow the polysaccharide to adsorb onto the protein monolayer as a complexing secondary layer. For convenience of identification, we may

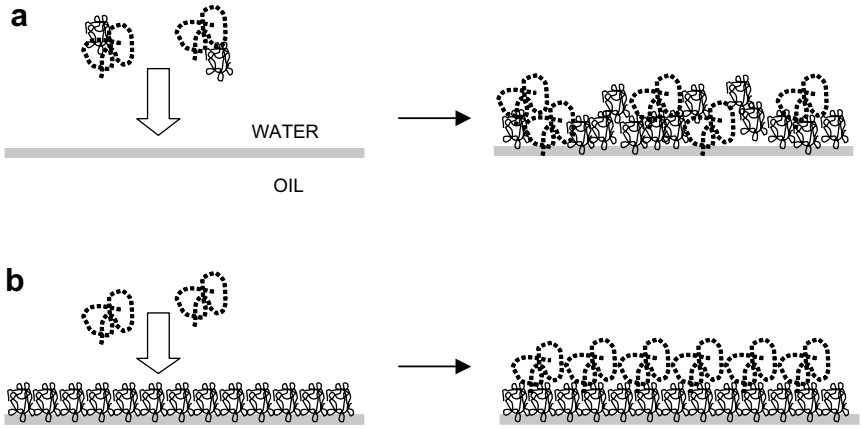

Fig. 7. Illustration of two alternative ways of making a composite layer composed of protein–polysaccharide complex at the oil–water interface: (a) the complex previously formed in solution adsorbs at bare interface; (b) the polysaccharide adsorbs onto a previously formed protein monolayer.

designate these two kinds of systems as (a) 'mixed emulsions' and (b) 'bilayer emulsions' (Jourdain, Leser, Schmitt, & Dickinson, 2008a, 2008b). Looking ahead to the future, there is good potential for use of such mixed interfacial layers in emulsions containing hydrocolloids in the development of delivery vehicles for nutrient encapsulation, and also in the protection of adsorbed proteins and emulsified lipids against enzymatic breakdown during digestion (Dickinson, 2008b).

Finally, it may be noted that the bilayer concept is not limited to just protein + hydrocolloid systems: it can be applied also to the case of electrostatic interaction between an adsorbed ionic surfactant in the primary layer and an oppositely charged hydrocolloid in the secondary layer (Nilsson & Bergenståhl, 2007b). Furthermore, the concept can be extended to more complex multilayer systems containing three (or even more) different layers (e.g., surfactant–protein–polysaccharide) (Bergenståhl, Fäldt, & Malmsten, 1995; Guzey & McClements, 2006). Further research activity on the properties of these mixed and bilayer formulations can be confidently anticipated over the next few years.

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