

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.

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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 nutraceuticals (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, & Ramaswamy, 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 $\sim 10 \mu\text{m}$ (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 $1 \mu\text{m}$ using an emulsifier which reduces the interfacial tension to $\gamma \sim 5 \text{ mN m}^{-1}$. From thermodynamics, we can estimate that the theoretical work associated with making the new interface is $\Delta G \sim 10^3 \text{ J m}^{-3}$. But in practice the actual amount of work required to make such an emulsion is of the order of 10^6 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 $10^{10} \text{ Pa m}^{-1}$ (i.e. 1 kbar 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

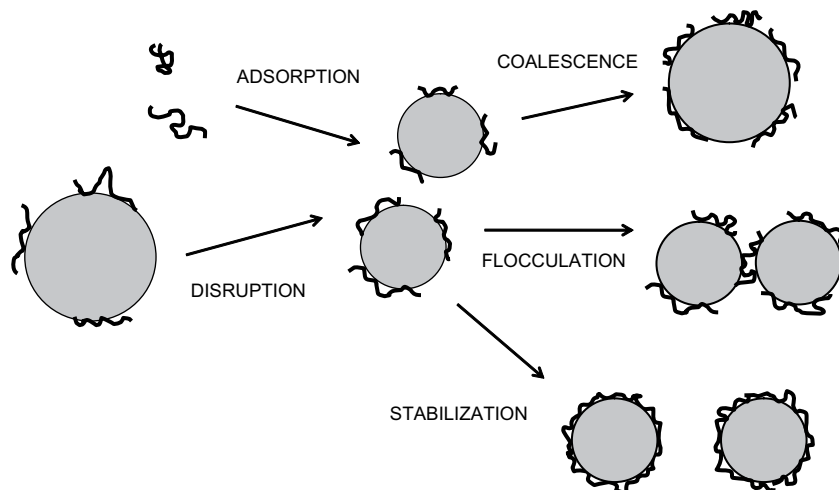


Fig. 1. Illustration of main physico-chemical processes involved in making of emulsions. Stabilization of fine droplets requires mechanical disruption of coarse droplets accompanied by rapid effective adsorption of emulsifier at the new oil–water interface. Collision of droplets with insufficient coverage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

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