Interfacial interactions and the stability of oil-in-water emulsions

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Abstract – Various aspects of the formation and stability of oil-in-water emulsions are described. Differences between adsorbed layers of proteins and small-molecule surfactants are considered, and influences of interfacial interactions and competitive adsorption are discussed.

INTRODUCTION

Oil-in-water emulsions are stabilized by two main types of molecular emulsifying agents: small-molecule surfactants and water-soluble polymers. In complex emulsions of commercial or technological importance, there often exists a multicomponent mixture of small amphiphiles and surface-active polymers. Emulsion structure, stability and rheology depends on the composition, thickness and viscoelasticity of the adsorbed stabilizing layer at the oil—water interface, and on the strength and nature of the interactions between adsorbed layers on different droplets. The stabilizing layer may also influence the crystallization behaviour of the dispersed phase and the kinetics of mass transport between droplets.

COMPETITIVE ADSORPTION

In food emulsions, the composition and structure of the interfacial stabilizing layer is determined by competitive adsorption between various proteins and small-molecule surfactants (lipids and lipid derivatives) (ref. 1 and 2). Competitive displacement of protein from the interface is observed experimentally (ref. 3—7) and predicted by theory (ref. 8) and computer simulation (ref. 9). Competition between individual proteins depends on their relative concentrations, the relative flexibilities of the macromolecules, and the sequence in which they are exposed to the interface (ref. 10-13).

Emulsion stability with respect to creaming and coalescence depends on the droplet-size distribution, the state of aggregation of the droplets, and the rheology of the aqueous dispersion medium. The droplet-size distribution is mainly determined by the energy input during emulsification, as well as by the nature and amount of the emulsifying agent(s). One way in which emulsion droplets become aggregated is by the attachment of adsorbing macromolecules to more than one droplet at a time (so-called bridging flocculation). Destabilization by non-adsorbing polymers may also be induced through the mechanism of depletion flocculation.

The sharing of proteinaceous emulsifier between droplets can occur during emulsion formation or shortly afterwards as a result of competitive adsorption (ref. 14 and 15). That is, with a binary mixture of a surface-active polymer (e.g. casein) and a less surface-active one (e.g. gum arabic), one finds that it is not possible to make a fine unflocculated emulsion at certain emulsifier compositions and total concentrations. This behaviour is explained in terms of a partial displacement from the oil—water interface of the hydrophilic polymer (gum arabic) by the hydrophobic polymer (casein), leading to bridging flocculation of the droplets by the preferentially adsorbing protein. A recent Monte Carlo simulation (ref. 15) has demonstrated how, for a simple model system, bridging flocculation can occur with a two-component emulsifier mixture when it is absent when either pure emulsifier is present alone.

A disordered protein like β-casein is a much more efficient adsorber than a small-molecule emulsifier like Tween 20 (polyoxyethylene sorbitan monolaurate) because it saturates the oil—water interface at a much lower bulk concentration. At equilibrium, effective monolayer coverage is reached with the protein at a molar concentration some 10^3 or 10^4 times lower than for the surfactant. This greater thermodynamic affinity of protein for the adsorbed state leads to greater equilibrium lowering of interfacial tension than with the surfactant at the same low bulk concentrations. On the other hand, small-molecule emulsifiers generally give a lower equilibrium tension than proteins at high bulk concentrations. This is the thermodynamic basis for competitive displacement of protein by surfactant from the oil—water interface at sufficiently high emulsifier/protein ratios. Another difference between proteins and surfactants is in the kinetics of adsorption: there is a more rapid reduction in the interfacial tension with small mobile surfactant molecules than with adsorbing macromolecules. Mainly for this reason, emulsion droplets made with surfactant present are generally smaller than those made with protein alone. Large differences in time-scale are also evident when comparing the competitive adsorption behaviour of protein + surfactant and protein + protein systems. Milk proteins can be rapidly and completely removed from the emulsion droplet surface by high concentrations of water-soluble surfactants (ref. 5—7). In contrast, with the notable exception of the caseins (ref. 11), the ability of one protein to competitively displace another protein already adsorbed is both slow and limited in extent (ref. 2).

Mixed adsorbed films composed of protein + surfactant are much less viscoelastic than pure protein films. For instance, the addition of Tween 20 to β-lactoglobulin gives a dramatic reduction in the interfacial shear viscosity at a 1:1 emulsifier-to-protein molar ratio, whilst the same relative Tween 20 concentration leads to no significant change in the amount of protein adsorbed at the emulsion droplet surface (ref. 5). It appears that the adsorbed surfactant acts as a sort of lubricant between the adsorbed protein molecules enabling them to flow past one another at the interface much more easily. In emulsions containing a mixture of proteins (e.g. α-lactalbumin + β-lacto-globulin), it seems that the kinetics of competitive protein exchange between the bulk aqueous phase and the oil—water interface is facilitated by the presence of the small-molecule surfactant (ref. 6).

OIL CRYSTALLIZATION AND MASS TRANSPORT

The state of crystallinity of oil droplets in emulsions can affect their state of aggregation to a substantial degree. Low-intensity ultrasound velocity measurement provides a sensitive way of determining whether oil droplets are liquid or solid at a particular temperature (ref. 16—18) since ultrasound velocities in liquid and solid oils may differ by a factor of two. The ultrasound velocity technique is non-invasive and convenient (ref. 19), and is particularly suited to studying systems as a function of time and temperature without mechanically disturbing the sample. Ultrasound is also useful as a probe of volume fraction, particle size and creaming behaviour in high-volume-fraction emulsions (ref. 19—22).

At concentrations above the critical micelle concentration, a surfactant like Tween 20 may assist mass transport of oil between emulsion droplets by solubilization of oil into surfactant aggregates in the aqueous phase between droplet surfaces. Conversely, proteins are unable to solubilize hydrocarbon molecules in solution to any significant extent, and the thick protein layer further inhibits mass transport between droplets by preventing colliding droplet surfaces from getting close together. Support for these views comes from recent experiments (ref. 23) on binary emulsions produced from equal proportions of n-hexadecane and n-octadecane droplets, which were prepared separately and mixed after homogenization. Oil crystallization in these binary emulsions was studied by ultrasound velocity measurement. With casein as the sole emulsifying agent, it was found (ref. 23) that the two sorts of oil droplets exhibit independent supercooling and crystallization behaviour—similar to that observed in the corresponding single oil emulsions. On the other hand, with a relatively high concentration of Tween 20 as the sole emulsifier, it was found that, on cooling, the onset of n-octadecane freezing is depressed by a few degrees, and that the freezing process, once it does occur, is not sharp (as for a pure oil) but takes place over a range of several degrees. The behaviour is indicative of intermixing of oils in the

n–hexadecane and n–octadecane droplets over a period of a few hours. Swollen Tween 20 micelles may act as a mode of transport for diffusion of n–hexadecane and n–octadecane molecules between droplets; in addition, some direct exchange may occur during the momentary collision of droplets.

Evidence for a direct interaction between the contents of droplets is provided by experiments on mixtures of solid and supercooled liquid droplets studied by the same ultrasound velocity technique (ref. 17). Over a period of several days, it appears that crystallization is induced in liquid n–hexadecane droplets when crystalline n–hexadecane droplets are mixed with them. There are two possible mechanisms for this. Protruding crystals on solid droplets could contact liquid droplets and hence induce nucleation in them. Alternatively, there could be a mechanism similar to Ostwald ripening whereby n–hexadecane molecules in the liquid droplets are transported through the aqueous phase into the solid droplets where they crystallize. The second process can probably be ruled out, however, since there is no significant change in droplet–size distribution at the conclusion of the crystallization.

COALESCENCE OF EMULSION DROPLETS

When emulsion droplets come close together, whether they will in fact coalesce depends on the stability of the thin liquid film of continuous phase separating them. Film rupture is a stochastic process driven by random thermal fluctuations. According to theory (ref. 24), the probability of rupture increases with the film diameter and decreases with the interfacial tension and the strength of the interdroplet repulsion. This may explain why proteins give good stability with respect to coalescence: they do not produce too low an interfacial tension, but are sufficiently surface–active to give small droplets, and the adsorbed layers are thick enough to give strong repulsion between droplets by steric stabilization. In addition, protein films are highly viscoelastic, and this tends to dampen down surface fluctuations, thus inhibiting the mechanism responsible for film rupture.

A correlation between coalescence stability and surface shear viscosity has been seen (ref. 25) in experiments with emulsion–sized droplets introduced into the vicinity of a planar oil–water interface aged with a pure protein. The proportion of droplets not coalescing with the interface within 24 hours was recorded. The order of stability (lysozyme > κ–casein > β–casein) correlates with the magnitudes of the surface shear viscosities of the aged protein films. With unaged protein films, where the surface viscosity is too small to measure, the rates of droplet coalescence are identical for each of the proteins within the statistical uncertainty.

At the protein concentrations encountered in food emulsions, the droplets are usually too stable for the coalescence rate to be measured by direct microscopic observation. Stability may be determined indirectly, however, by following changes in droplet–size distribution as a function of storage time. Enhanced steric stabilization of proteins may be achieved by complexation of proteins with high–molecular–weight polysaccharides via covalent or electrostatic interactions (ref. 26 and 27). The important factor here is that the protein–polysaccharide interaction should be strong to avoid possible problems of depletion or bridging flocculation, and that the complex should remain soluble in order to retain the good emulsifying properties of the protein.

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