Advances in FOOD EMULSIONS AND FOAMS

Edited by
ERIC DICKINSON AND
GEORGE STAINSBY

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ADVANCES IN FOOD EMULSIONS AND FOAMS

Preface

There has been much activity in the area of food emulsions and foams in the five years or so that have elapsed since we finished writing *Colloids in Food* (Applied Science Publishers, London, 1982). This volume represents our attempt to bring things up to date by collecting together what we feel to be some of the major recent developments, with the invaluable assistance of several of the most prominent workers in the field. The aim has been to produce an authoritative statement of the current limits to understanding. In editing a review volume in an active area of research like this, we are attempting, possibly in vain, to hit a moving target: the more time and trouble taken to assemble the material, the less immediately topical it is likely to be. In the end, only the individual reader can say whether we have achieved the right balance between topicality and critical assessment.

The basic principles are set out in the first three chapters. Whereas Chapter 1 deals primarily with protein-stabilized emulsions, Chapter 2 focuses on the role of low-molecular-weight emulsifiers, with particular emphasis on the distinction between surfactants that form monolayers and those that form thick multilayers. The link between Chapter 2 (emulsions) and Chapter 3 (foams) lies in the fact that film drainage and film rupture are phenomena common to both types of system. In Chapter 4, recent work on adsorbed protein films at fluid interfaces is reviewed, and its importance in relation to the formation and stability of food emulsions and foams is assessed. The optimization of the functional properties of food macromolecules is an important area of current research, and to reflect this the next two Chapters, 5 and 6, are devoted to a discussion of how emulsifying and foaming properties are

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affected by protein modification, either chemical (Chapter 5) or enzymic (Chapter 6). The properties of two important classes of food products, dairy foams and cream liqueurs, are reviewed in Chapters 7 and 8, respectively. The concluding chapters deal with two topics that seem likely to become increasingly prominent over the next few years. Chapter 9 describes in detail how new ultrasonic techniques are valuable for monitoring the properties of food emulsions and dispersions. And Chapter 10 addresses the intriguing question as to how low-molecular-weight food additives are distributed in colloidal systems.

We have made strenuous efforts to produce a volume that looks and reads like a coherent entity. In this, we are extremely grateful to the authors of individual chapters for their forbearance and care in dealing with the many queries and comments which we raised in connection with their manuscripts, both 'original' and 'revised'. To make for clarity and consistency of style, much of the original text has been slightly modified or rewritten, but without any distortion, we hope, of the underlying scientific meaning. If we have erred as editors, it will probably have been in the direction of doing too much, rather than too little. We apologize here to any author of an individual chapter who regrets that his own particular style of writing has been lost during the editing process.

E.D., G.S.

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Contents

Chapter 1

Emulsion Stability

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1.1 Introduction

The traditional definition of an emulsion — a colloidal dispersion of liquid droplets in another liquid phase — is too narrow to include most food emulsions. Salad cream, certainly, is an emulsion in the strictest sense, but many food emulsions are considerably more complex (Dickinson and Stainsby 1982). In the first place, the dispersed phase is more likely than not to be partially solidified, and to an extent which is quite strongly temperature dependent. Dairy products are in this category. Secondly, the continuous phase may also contain crystalline material, as in ice-cream; or it may be a gel, as in many desserts. In addition to this, air bubbles may have been incorporated in order to produce a light texture, as in whipped cream. Also, a good proportion of the droplets may be beyond the colloidal size range. Some meat emulsions contain fat particles of visible dimensions: they are excluded from consideration here as their stability is not governed primarily by the properties of and the interactions between the dispersed particles.

There are several reasons why food emulsions are important to the food manufacturer. A major consideration is the improvement in palatability, mouthfeel, texture and general appearance in systems containing both oil and water. Olive oil on its own may be too greasy to the taste, but it becomes widely acceptable in an emulsified oil-and-vinegar salad dressing. The two immiscible liquids are both required because some flavour ingredients are insoluble in the salad oil, whereas others are insoluble in the vinegar. (The partitioning of flavour ingredients and other additives between immiscible phases is considered

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in Chapter 10.) In addition to flavour considerations, the use of a relatively high volume fraction of dispersed oil phase leads to a thick creamy product without the necessity for large quantities of thickener or gelling agent.

The creation of a *bona fide* food emulsion involves disrupting the dispersed phase into droplets of colloidal size, and protecting the newly formed droplet interface from immediate coalescence. An emulsifier has, firstly, to facilitate the production of a new interface by lowering the interfacial free energy, and, secondly, to provide short-term stability by forming a protective adsorbed layer at the oil–water interface. Commercial food emulsifiers are generally a mixture of components. There are two broad classes: macromolecules, and permitted low-molecular-weight amphiphiles (Spans, Tweens, etc.). In addition, since their breakdown products (mono- and diglycerides) are surface-active, food oils almost invariably provide additional components that can act in an emulsifying capacity. Although macromolecules are less surface-active than low-molecular-weight amphiphiles, and are adsorbed less rapidly (see Chapter 4), many food proteins are useful emulsifiers. But only a few polysaccharides are sufficiently surface-active (Darling and Birkett 1987).

Regrettably, there is still some confusion in technological usage between the terms 'emulsifier' and 'stabilizer'. A useful distinction can be made in terms of stability. An emulsifier must confer short-term stability, since this is essential for the preparation of all emulsions. With some emulsions (e.g., cake batter or ice-cream mix), a lifetime of hours or even minutes is all that may be required. Other products (e.g., cream liqueurs or mayonnaise) may need to remain stable for several years, and for these a stabilizer is required. Long-term stability of oil-in-water emulsions may be achieved by thickening the aqueous phase or adsorbing a film of polymer molecules on the aqueous side of the oil–water interface. Most polysaccharides acts as stabilizers through their modification of the rheological properties of the aqueous dispersion medium. Proteins, on the other hand, act primarily through the properties of their interfacial films, and are therefore both emulsifiers and stabilizers in many instances. Water-in-oil emulsions such as butter and margarine are mainly stabilized through the network of fat crystals in the semi-solid continuous phase.

The droplets in food emulsions are widely dispersed in size, and may range from 0·1 μm to 10 μm in any one system. Proper characterization

of this droplet-size polydispersity is a formidable problem. Dynamic light-scattering methods that are suitable for sizing particles of diameter 0·1 μm may be totally inadequate for sizing particles of diameter 10 μm, and vice versa for techniques such as optical microscopy or Coulter counting. The consequence of this is that there is often difficulty in adequately checking the reproducibility of manufacture. In practice, most attention tends to be focused on the top end of the size distribution, on the basis that most types of instability are usually first manifested in the behaviour of the largest droplets.

As well as droplet-size polydispersity, there may also be considerable heterogeneity in the nature of the adsorbed films around the emulsion droplets. This is particularly the case in the production of a wide range of dairy emulsions from milk or cream. Emulsification involves disruption of the natural membrane around the milk-fat globules, and the creation and stabilization of new droplets. In the final product, some of the very small droplets, which have not been disrupted by the flow field, will still be stabilized entirely by the natural membrane. Other droplets may be stabilized entirely by the added emulsifier, or by a combination of added emulsifier and natural membrane. Furthermore, some of the natural membrane is likely to be distributed within the bulk aqueous phase, where it may aggregate and no longer be capable of adsorption. Indigenous enzymes originally present in the membrane may be released during emulsification, and these may affect the long-term stability by catalysing chemical changes and promoting macromolecular degradation.

The purpose of this chapter is to assess recent progress in the understanding and characterization of food emulsion stability, and to provide an appropriate introduction to what follows later in this volume (especially Chapters 2, 5, 6, 8 and 9). The emphasis will be on recent advances in experimental information and theoretical understanding. In relation to basic theory, we shall not cover old ground, but simply remind the reader of the more salient points as we see them. The general principles of emulsion formation have been set out fairly recently by Walstra (1983), and the concepts underlying the stabilization of emulsions by macromolecules are covered in detail by Dickinson and Stainsby (1982) and Tadros and Vincent (1983). For recent reviews of the physico-chemical factors affecting emulsion structure and stability, the reader is referred elsewhere (Dickinson 1987a, 1988, Melik and Fogler 1988).

As a prelude to our discussion of the various primary processes of emulsion stability, we shall first consider some relevant aspects of manufacture.

1.2 Emulsion Formation

Emulsion manufacture is a highly energetic and dynamic process. Coarse emulsions can be made by vigorous stirring. Fine emulsions are normally made using a high-pressure homogenizer, the basic design of which was introduced some 80 years ago. Other techniques for emulsification include sonication and colloid milling. Tornberg (1978) has compared the various methods for making protein-stabilized emulsions using laboratory-scale equipment, and has shown how the particle size can vary with the experimental conditions and the type of equipment being used.

When the amount of emulsifier available is strictly limited, as is the case with highly purified proteins, the experimenter is restricted to making emulsions on a very small scale. Until recently this has almost invariably meant the use of an ultrasonic technique, even though such a method is never used commercially. To get round this problem, a high-pressure mini-homogenizer has been developed (Dickinson *et al.* 1987b) which produces emulsions of similar particle-size distribution to that of emulsions made with a commercial laboratory-scale valve homogenizer, which requires at least 20 times more emulsifier. The main experimental difficulty in using a valve homogenizer when only small volumes are involved lies in the preparation of a stable, uniform feedstock (the 'premix') which is free from incorporated air.

In the new method of emulsification called 'microfluidization', based on technology originating at Arthur D. Little, Inc. (U.S. Patent 4 533 254), the premixing stage is eliminated. Separate streams of oil and aqueous phase are accelerated to high speeds (up to 50 m s^{-1}), mixed, and then guided to an impingement area where effective emulsification occurs. One feature of the microfluidization method is that there are no moving parts. Another is that, although the energy of the moving streams is released extremely rapidly, the process is nevertheless gentle enough, apparently, for enzymes to remain native. Temperature control is essential, but this is readily achieved using a heat exchanger, or, on the laboratory scale, by submerging the unit in a constant temperature bath. It is claimed by the manufacturer that very fine emulsions can be made

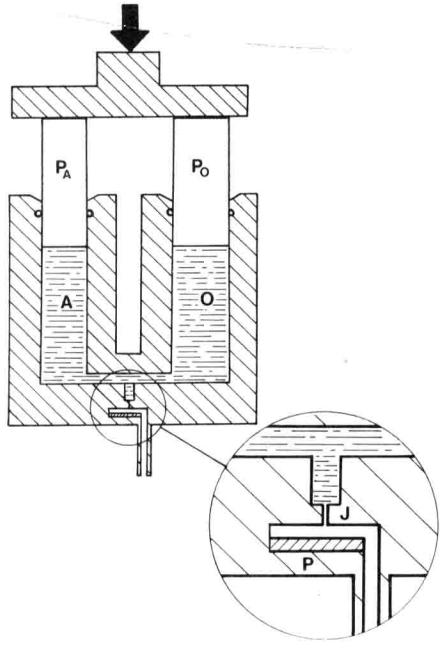

Fig. 1.1. Schematic diagram of the jet homogenizer (not drawn to scale): A = aqueous protein solution; O = oil; P_A = piston A; P_O = piston O; P = fixed plate; J = 'jet' hole (0·4 mm diameter). Compressed air drives pistons P_A and P_O in the direction of the arrow.

with narrow particle-size distributions. Korstvedt *et al.* (1984) have demonstrated the potential of the method for producing mineral oil emulsions with a blend of non-ionic surfactants. (Even when no surfactant is added, a 10 wt% vegetable oil emulsion is fine enough to remain stable for 2 days.) Castle *et al.* (1988) have used a similar experimental arrangement (see Fig. 1.1) to produce coarser protein-stabilized oil-in-water emulsions (55 vol%).

The high-pressure valve homogenizer is still the most widely used method for manufacturing food emulsions. Droplets are disrupted by a combination of intense laminar and turbulent flow (Walstra 1983, Phipps 1985, Davies 1985). The main factor affecting the emulsion droplet-size distribution is the pressure drop across the homogenizer valve, and increased turbulence on the low-pressure side of the valve favours the formation of finer emulsions. By way of contrast, differences

in interfacial tension provide only a relatively small degree of control over droplet size. If the premix viscosity is high, only a coarse emulsion can be formed unless the operating pressure is raised substantially. Under conditions of turbulent flow, casein micelles are adsorbed at the oil–water interface more rapidly than the monomeric caseins (Walstra 1980). In the same way, one expects the less voluminous aggregates of caseinate or globular proteins to adsorb preferentially over their monomeric constituents.

1.3 Interfacial Composition and Competitive Adsorption

Whatever is the method used to make an emulsion, there is likely to be competition between the various surface-active components for adsorption at the newly created interface. There is competition, firstly, between the various low-molecular-weight surfactants, whether deliberately added or inevitably present in the oil, and also, secondly, between these surfactants and the various macromolecular components, which may differ in composition (caseinate), in molecular size (gelatin), or in state of aggregation (soya). The concentrations of the added surfactants are limited by law. The concentrations of the macromolecular emulsifiers are usually set high in order to produce the required high rate of adsorption. It follows that only a fraction of the potentially available emulsifier is actually present at the interface. In some cream liqueurs, for example, about one half of the added protein emulsifier remains in the continuous phase (Narhan 1987). As a general rule, because of competitive adsorption, the chemical composition of the interface will rarely match that of the ingredients prior to emulsification.

Over the last few years, there have been important advances in the area of competitive adsorption, particularly as it applies to proteins at the oil–water interface. To put these results in context, however, it is appropriate first to recall briefly the molecular properties that are necessary for an effective emulsifier.

With low-molecular-weight amphiphiles, an important attribute is the HLB value for the blend. In practice, the optimum HLB value can vary to some extent with the chemical nature of the oil phase, and so it is better to optimize the composition of an emulsifier blend by experiment rather than by calculation. An emulsion is most effectively stabilized when a drop of the oil phase just fails to spread on the surface of the emulsifier solution (Ross *et al.* 1959). This simple approach has been

used by Chilton and Laws (1980) to evaluate Spans and Tweens for emulsifying hop oils.

A key requirement with proteinaceous emulsifiers is adequate solubility (Halling 1981). This is not always easily achieved — particularly when the pH is not far from the isoelectric region, or when the protein is extensively aggregated. Improved solubility is an important motivation behind the chemical and enzymatic modification of food proteins (Jimenez-Flores and Richardson 1987).

The main molecular requirements for a protein emulsifier are backbone flexibility and sufficient hydrophobicity. Proteins that score well on both counts are α_{s1}- and β-casein, the major components of caseinate, which is still the most extensively used emulsifier and emulsion stabilizer in the food industry. Most food proteins are, of course, globular in their native state, and so it is not unexpected that the experimental *surface* hydrophobicity is of more consequence* than the overall molecular hydrophobicity as determined from the amino-acid composition. A correlation for several globular proteins between emulsifying activity and surface hydrophobicity was first demonstrated by Kato and Nakai (1980), and the same trend has since been confirmed for a wide range of proteins, both native and denatured (Kato *et al.* 1983, Li-Chan *et al.* 1984), though there are exceptions to the rule. For instance, Shimizu *et al.* (1985) report that the surface hydrophobicity of β-lactoglobulin is much greater at pH 3 than it is at pH 7, yet the rate of adsorption, as determined from the surface pressure (see, however, Chapter 4), is much slower at the lower pH. Moreover, as the pH was reduced, there was an increase in emulsion droplet size as determined by the turbidometric method of Pearce and Kinsella (1978). It is suggested by Shimizu *et al.* (1985) that the resistance to denaturation increases in acidic solutions, and that this is the most important factor. Certainly, an ability to lose tertiary structure is a positive attribute for a proteinaceous emulsifier, and this can be reflected in the adsorption behaviour at planar oil–water interfaces (Chapter 4). Providing solubility is not adversely affected, heat denaturation improves

*Surprisingly, even for the disordered caseins, the calculated *overall* hydrophobicities do not correlate with their separation *via* hydrophobic interaction chromatography (Chaplin 1986). Though this result could be interpreted to mean that at least some regions of the caseins have an ordered secondary structure, which makes the surface hydrophobicity different from the overall hydrophobicity, it may also be that the nature of the protein–substrate interaction in hydrophobic interaction chromatography is not simply hydrophobic!

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