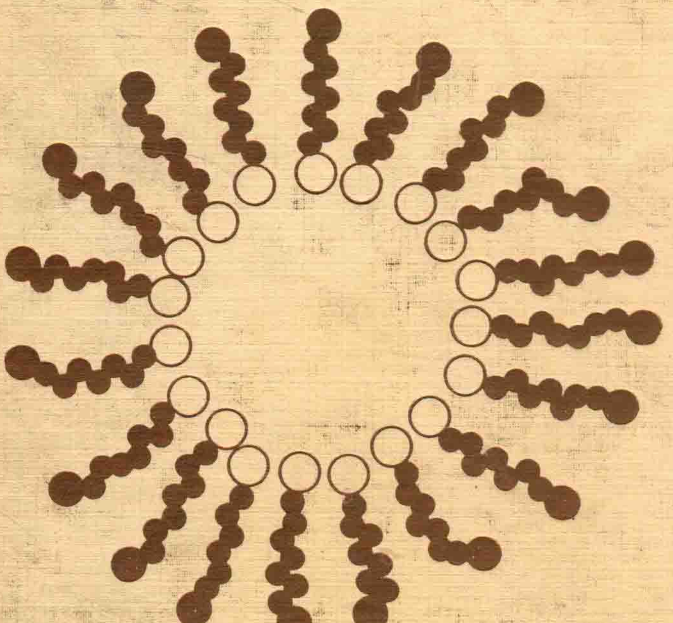
Microemulsions and Emulsions in Foods



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Microemulsions and Emulsions in Foods

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Foreword

THE ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset, but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the editors with the assistance of the Advisory Board and are selected to maintain the integrity of the symposia. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation. However, verbatim reproductions of previously published papers are not accepted.

Preface

THE FIELD OF FOOD EMULSIONS HAS ALWAYS GENERATED great interest. However, little has been done with microemulsions applicable to the complex world of foods. Microemulsions have been the subject of much fundamental research that focuses on noningestible systems. For example, applications to nonfood uses such as tertiary oil recovery, fuel, cosmetics, and household products has received considerable attention.

The purpose of this book is to bring together the two related disciplines of emulsions and microemulsions in an attempt to foster new developments and new directions for fundamental research. Although the book is intended primarily for technologists in the food industry and researchers in academe, much of the knowledge contained herein may be directly applicable to cosmetics, pharmaceutical areas such as health care or drug delivery, and stabilization of lotions and creams.

The introduction, written by Paul Becher, analyzes the book's chapters, and the overview by Stig Friberg and Ibrahim Kayali examines the physical differences between microemulsions and emulsions.

The first section of the book covers microemulsions in foods. The scientific literature contains little information on microemulsion systems directly applicable to foods. Kare Larsson's monoglyceride/water/oil system was the first practical system to be published. Other chapters describe synthesis in microemulsion media and preparation of microemulsions and phase diagrams.

The final section of the book looks at emulsions in foods. The phase behavior of sucrose esters is discussed, and the emulsion stabilization properties of newly synthesized polypeptides are reported. The largest share of the book is on emulsions stabilized by proteins: protein–emulsifier and protein–protein interactions and their effects on interfacial films. Stabilization of emulsions by polysaccharide is also represented. Novel nondestructive methods for measuring emulsion stability, with broad applications in emulsion technology, are described.

Overall, the book covers many of the more innovative approaches to emulsion stability in foods, presents the results of some initial investigations into food microemulsions, and compares the two types of systems. It is hoped that the book will inspire others to continue the investigation of food microemulsions.

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We would like to thank each of the contributing authors for their cooperation, without which there would not have been a book. Many thanks to the editorial staff of the ACS Books Department, especially to Cheryl Shanks and Barbara Tansill. Last but not least, we would like to acknowledge with thanks Carla Cobb and Pat Greene for their secretarial support.

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Chapter 1

Food Emulsions

An Introduction

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In this introduction the long history of food emulsions is first contrasted with the comparatively short time over which they have been subject to scientific study. The contrasting degree of interest in macro– and microemulsions in the food industry is discussed, and the various ways in which such emulsions may be studied is considered. Finally, the various aspects of this symposium are considered, as well as the role which some of the contributions may play in the progress of this discipline.

It is an interesting fact that the first food emulsion we encounter during our lives is also probably the oldest — namely, milk. Mammalian life is first encountered several billion years after the Big Bang, probably of the order of one hundred million years ago, and, with mammals, comes milk. In Table I I have presented a short (and, obviously, abbreviated) history of food emulsions. However abbreviated, it is nonetheless useful as indicating that the subject of this symposium does have a long history.

However, in spite of this long history, the scientific study of emulsions in general, and food emulsions in particular, is a fairly recent phenomenon. The word *emulsion* dates from the first years of the 17th century (although not precisely with the current connotation), but the scientific investigation is little more than a century old; indeed, the classification of emulsions as oil-in-water or water-in-oil dates from a 1910 paper by Wolfgang Ostwald [1].

It would be even more correct to say that the true theoretical under-pinnings of emulsion theory could not exist until after the post-WWII development of the theory of the electric double layer, the DLVO theory [2].

Even more recent, of course, is the concept of the microemulsion, dating from Schulman and Montagne in 1961 [3]. Although the title of this symposium is,

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Table 1: A Short History of Food Emulsions

FOOD	DATE OF INTRODUCTION
Mammalian Milk	c. 2.4×10^7 BC
Milk from Domestic Animals/Butter/Cheese	c. 8500 BC
Sauces	15th–16th Century
Ice Cream	c. 1740
Mayonnaise	c. 1845
Margarine	1869

in fact, *Microemulsions and Emulsions in Foods*, and, although many of the papers included in the symposium are on various aspects of microemulsions, I suspect that we will find that this is a new field, with much to be said for the future, but little we can say about the past.

In fact, in preparation for writing this paper, I did a quick and dirty computer search based on the simple research strategy

`food? and microemulsion?`

The yield from this search was a mere four references (two to patents), none older than 1987. On the other hand, the search strategy

`food? and emulsion?`

yielded no less than 475 hits.

I should point out, in addition, that a recent review of applications of microemulsions contained but a single reference to foods [4].

In fact, a number of recent books on food emulsions, edited by, respectively, Friberg (1976) [5], Dickinson (1987) [6], and Dickinson and Stainsby (1988) [7], contain no instances of food microemulsions (except for one minor reference in [6]).

This lack of interest may possibly be ascribed to a number of related factors. First, the high levels of emulsifying agents normally encountered in microemulsions quite simply serves as an economic barrier. Second, this same high level of emulsifier might well raise legal problems in securing approval from the FDA. Third, of course, there is the simple fact that it is apparently quite difficult to make microemulsions of the fats and oils used in foods.

Why, then, a symposium on *Microemulsions* and Emulsions in Foods? As far as *macro*emulsions are concerned, the considerable activity noted above is reason enough – we simply want to keep posted. On the other hand, the inclusion of micro emulsions is a matter of looking to the future. Is there, in fact, a role for microemulsions in the food industry, and, if so, what do food technicians have to know about this topic?

The editors have chosen, logically enough, to order the papers in this symposium as follows:

- Introduction (this paper)
- Overview
- Microemulsions in Foods
- Emulsions in Foods

For the purposes of this introduction, however, I would like to consider the various contributions in a slightly different way:

- Micro– and macroemulsions, without specific reference to food, serving as background.
- Food emulsions, principally (but not exclusively) macroemulsions.
- Food emulsifiers, their properties or production.

Following the lucid overview of Friberg and Kayali (which defines further the distinctions between micro– and macroemulsions, and illuminates the difficulties involved in the application of microemulsions to foods alluded to above), in the first category, we may single out the papers of Larsson; El-Nokaly; Osborne, Pesheck, and Chipman; and Biais, Bothorel, Clin, and Lalanne. In particular the last of these connects the concept of the influence of the bending energy with stability in microemulsions. This was also touched upon by Friberg and Kayali, which with the papers in this group, provide an introduction (albeit a brief one) to the problems associated with microemulsions and their formulation.

There is more meat (if one may be permitted a gustatory pun) in the second category. The interaction between protein and emulsifiers (a significant effect in many food emulsions) is discussed from various points of view by Dickinson; Martinez Mendoza and Sherman; Westerbeek and Prins; Li-Chan and Nakai; and by Makino and Moriyama. It is interesting to note that in various of these papers the investigators have favored a different research technique, in all cases with illuminating results. Two other papers, one by Goetz and El-Aaser, the other by Robins, are also concerned with investigative techniques; the former uses electroacoustic measurements to determine ζ–potentials, while the latter employs an ultrasonic monitor to follow creaming.

In the final category, there useful papers on the synthesis of monoglycerides in microemulsion (Mazur, Hiler, and El-Nokaly); sucrose esters, describing their L_2 phases (Herrington, Midmore, and Sahi); liposarcosine polymeric surfactants, which form microemulsions with the formation of liquid crystals (Gallot); protein–dextran hybrids (Kato and Kobayashi); and stabilizers for milk–derived vesicles (Whitburn and Dunne).

As my own contribution to this symposium, I would like to include a few words on the subject of research in foods.

In view of the lengthy history of food emulsions detailed in Table 1, the relatively recent attention to the theory of food emulsions is illustrated by the classic 1946 paper of Corran [8] on mayonnaise. Corran investigated the effect of the egg-yolk composition (lecithin-cholesterol ratio), phase volume, emulsifying effect of the mustard (effect of fineness), method of mixing, water hardness, and the viscosity of the finished product. Although Corran's methods were primitive by today's standards, the completeness of the study can stand as a paradigm for the investigation of food emulsions. This paper, or the summary in Becher [9], may still be referred to usefully.

Although the composition of mayonnaise is strictly regulated by law, it should be pointed out that true mayonnaise aficionados claim to be able to distinguish between various commercial brands. Verification of this, and, if true, an explanation, would represent a proper homage to Corran, as well as a significant piece of food research.

As another significant bit of food research (even if tongue–in–cheek), would be the famous exchange of papers regarding the application of DLVO theory to Béarnaise sauce [12].

The study of food emulsions may be considered to have followed three paths:

- Physico–chemical studies of the whole emulsion system, e.g., effect of composition on stability, rheology, color, taste, etc.
- Physico–chemical studies of model systems, e.g., surfactant interactions with other components, etc.
- Formulation of finished emulsion products, including consumer test panel evaluation, packaging studies, etc.

On the first such path, the food itself has been the subject studied (as done by Corran), e.g., milk, ice cream, cake emulsions, meat emulsions, etc. On the second path, model systems have been investigated, although these studies have often been limited to a single interaction, e.g., water with lipids, surface-active agents with protein, etc. A number of examples of this approach will be found in the present symposium.

A third path may be considered to exist: I refer to the actual formulation of food systems, wherein, one may hope, the formulator is guided by the lessons derived from the first two paths.

As an example of the first route we may consider milk One may possibly be surprised to see such an ancient system as milk (Table I) listed as those subject to investigation A large part of the studies on milk, of course, have been devoted to homogenization [10]. (I wonder how many of this group remember the days of *un*homogenized milk, when there was a premium in rich coffee cream for the first one up!), with possibly as much attention devoted to the nature of the milk interface [11].

I should emphasize, also, that in food emulsions the relation between the properties of the emulsion and its texture (e.g., mouth feel in such systems as ice cream) is also a major area for investigation.

The second route particularly is exemplified by numerous studies of the behavior of proteins and surfactants at the oil/water interface, of which excellent examples are to be found in the recent literature [6, 7].

As for the third route — formulation — the results of these investigations will be found widely throughout the patent literature, and, of course, on the shelves of your local supermarket.

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Chapter 2

Surfactant Association Structures, Microemulsions, and Emulsions in Foods

An Overview

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A great variety of dispersants are employed in food emulsions ranging from hydrotropes to solid particles. However, surfactant association structures, micelles, and lyotropic liquid crystals are of decisive importance for the properties of food emulsions and their response during the absorption of lipids in the stomach. Examples are provided demonstrating the use of hydrotopes and lamellar liquid crystals to form microemulsions with liquid triglycerides. In addition the importance of liquid crystals for emulsion is demonstrated.

Emulsions are well known in food science and several monographs have focused on this theme (1-3). A large variety of stabilizers are used to obtain optimal properties to the emulsions depending on the final product (4). In addition the application of specific stabilizers is related to the natural origin of food products; in fact some emulsions are of biological origin.

Such an emulsion is milk, a 4% fat O/W emulsion is an aqueous phase with a few percent protein and lactose. It is stabilized by a lipid protein membrane, whose structure has been extensively investigated (5-7). The early suggestions of a combination of a phospholipid bilayer and proteins (7) appears to have stood the test of time. However, milk in its native state is not available commercially and the research has focused on changes in the membrane due to processing (8). The kinetic interfacial processes with the competition for surface sites between proteins and lipids have generated a research using different approaches (9,10). Other food dispersions (4) stabilized by proteins are ice cream (caseinate), cake batter (whey protein), and mayonnaise (egg protein). Polysaccharides are another natural protein applied to artificial creams and salad dressings.

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