Food Emulsion and Foams: Theory and Practice

Peter J. Wan, volume editor

John L. Cavallo, Fouad Z. Saleeb and Michael J. McCarthy, volume coeditors

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FOREWORD

In 1988, we were asked to organize a Food Emulsion Symposium for the AIChE Annual Meeting in San Francisco, November 5–10, 1989. We started with the idea of including all three components, namely, theory, methods and applications, in one symposium. Soon we realized that there was too much to be covered in one session. Finally, the topics were divided into two separate symposia. One dealt with theoretical subjects of food emulsion. The other covered selected practical examples of food emulsions.

The speakers were from both academic and industrial sectors. All the speakers committed to these symposia had a common understanding that there is a need for a food emulsion publication. The feeling grew stronger after the AIChE meeting. At the same time, we discovered that a very good symposium on foam was also presented during the same convention. After several communications with the symposium chairmen and speakers, a proposal to combine food emulsion and foam in one volume was soon approved by the AIChE Symposium Series Editor.

The focus of these symposia is to demonstrate the importance of surface and colloid science in food systems. The topics covered the interfacial properties of emulsifier and protein films, phase science of food emulsifiers, formulation considerations in emulsion systems; oil-in-water (O/W), water-in-oil (W/O) or air-in-liquid (A/L), interfacial rheology, foam rheology, foam stability, and water mobility in foam systems. Design and selection of food emulsifiers, principles of emulsion films and examples of several food emulsions, such as, margarine, low fat spreads, and ice creams were also presented.

The state of the art of methodologies and hardware were presented at the symposium but failed to make this publication. We sincerely hope that this volume provides a better understanding on food emulsions and offers some useful ideas on such complex food systems to the readers. We also wish to express our gratitude to all our speakers, authors and reviewers who made this publication a successful and meaningful task.

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CONTENTS

INTERFACIAL PROPERTIES OF EMULSIFIER/PROTEIN FILMS RELATED TO FOOD EMULSIONS

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In many food emulsions the fat globules are stabilized to prevent coalescence by an adsorbed protein film. When emulsions are aerated (creams, toppings, ice cream mix) the protein film is partially removed by mechanical shear forces during whipping. The increased hydrophobicity of the fat globules causes them to be adsorbed at the air/water interface during aeration. The air cells of the final foam are thus covered by a layer of flocculated fat globules, and fat crystals may be present as well. The stability, firmness and texture of the foam are determined by the interconnecting shells of fat particles that it contains. In the case of ice cream, partial protein desorption from fat globules takes place during the ageing of the mix before freezing. This desorption is enhanced by emulsifiers, which change the interfacial film properties when the emulsion is cooled. The present study shows a correlation between the protein desorption from the fat globule surfaces and the interfacial film properties of oil/water systems containing monoglycerides and proteins.

Many food emulsions are stabilized by proteins, which form a protective layer round the fat globules. In aerated emulsions such as ice cream, frozen desserts, whipped cream and toppings the air cells are stabilized by adsorbed fat globules, fat crystals and proteins. In simple milk foams the air cells are covered with milk casein micelles, which stabilize such foams (1). During the aeration of cream the initial foam formation is also created by the proteins which are present, but on continued whipping fat globules become increasingly adsorbed at the air/serum interface together with fat crystals from mechanically disrupted fat globules. The air cells are thus predominantly stabilized by fat globules or crystals in such foams. Whipped toppings based on high lauric type fats undergo a complete structural change during reconstitution and whipping, resulting in a foam stabilized mainly by fat crystal platelets at the air/serum interface (2).

Food emulsifiers are used to control the destabilization of such emulsions, and their main function is to promote desorption of inter-facially-bound protein, making the fat globules more hydrophobic, increasing their affinity for air, and thus enhancing their adsorption at the air cell interface (3). A correlation between a decrease in interfacial tension and an increase in fat destabilization in the presence of emulsifiers has been described in the literature (4). In order to study the functions of monoglycerides further, interfacial tension measurements of oil/water systems similar to whippable emulsions have been studied at temperatures corresponding to the processing conditions for ice cream in an attempt to explain the role of emulsifiers in whipped emulsions in greater detail.

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THE ADSORPTION OF PROTEINS

Protein molecules may adsorb to oil droplets with several segments of the same molecule in contact with the oil phase and other more hydrophilic segments arranged in the bulk water phase. If the oil contains surface-active lipids, such as monoglycerides, which adsorb more rapidly than proteins, these lipids may provide an energy barrier against protein adsorption, and thereby influence the amount of protein adsorbed (5).

In general, the function of proteins is to give steric stabilization of emulsions against coalescence, and their relative effect depends on their solubility and surface activity. Small globular proteins such as bovine serum albumin and lysozyme are highly soluble but limited with regard to surface activity, whereas large hydrophobic proteins (such as heat-denatured proteins) are sufficiently surface-active but limited with regard to solubility. The best compromise is proteins such as sodium caseinate which are both highly soluble and surface-active.

Casein in milk consists of four types of proteins known as α-s1, α-s2, ß, and κ-casein, which are present in the ratio 4:1:4:1. They can be co-precipitated at pH 4.6 and made soluble by forming sodium caseinates. It has been found that α-s1 and ß-caseinates are equally adsorbed during homogenization, but on ageing ß-casein replaces some but not all surface-bound α-s2 casein (6). ß-casein is also found to be the most surface-active and the most hydrophobic of the milk proteins. When using skimmed milk for making emulsions (recombined milk), all the caseins are adsorbed onto the surfaces of oil droplets in the same proportions as in milk (7). Under such conditions caseins are adsorbed as micelles, and it is found that large micelles (up to 300 nm) are adsorbed in preference to small micelles or serum proteins (8).

An important factor for steric stabilization of oil droplets is the amount of protein adsorbed at the surface, the so-called surface load, normally expressed in mg protein per m^2 surface area of emulsified oil. The protein load may vary considerably in o/w emulsions, e.g. from 1 mg/m^2 (roughly corresponding to a monolayer of extended unfolded polypeptide chains) to several times 10 mg/m^2 (9). A surface load of approx. 3 mg/m^2 corresponds to a monolayer of globular proteins or partly unfolded protein molecules adsorbed in loops and trains. If the surface load is greater than 5 mg/m^2, the protein layer consists of aggregates or multilayers. The surface load varies, depending on the concentration of protein in bulk solution and on the oil surface area formed during emulsification. The proteins of skimmed milk display complete adsorption up to a surface load of about 8 mg/m^2, which is a saturation point. Whey proteins and sodium caseinate have a saturation point of about 2.5-3 mg/m^2.

In food emulsions such as ice cream mixes,proteins and emulsifiers as well as hydrocolloids (gums) are usually all present, and these components all take part in forming the surface film around the oil droplets. The emulsifiers are usually monoglycerides or blends of monoglycerides and polysorbates in a ratio of about 4:1, and the emulsifiers are more surface-active than milk proteins or gums. Consequently, the emulsifiers will be adsorbed in preference to the o/w interface due to their higher adsorption energy, and thereby influence the adsorption of proteins. A reduction in protein load of as much as 50% has been found when highly polar emulsifiers such as polysorbates are used (4).

CONTROLLED DESTABILIZATION OF WHIPPABLE EMULSIONS

The structure of aerated emulsions such as ice cream, whipped cream and toppings consists of air cells distributed uniformly in a frozen or liquid continuous phase containing carbohydrates, proteins and fat globules. The texture and stability of the whipped product is related to the air cell structure, which is built up by shells of fat globules or crystals arranged at the interface between air and water.

Figure 1. The structure of the air cell/serum interface in a whipped imitation cream by transmission electron microscopy using freeze fracture technique. S = serum phase, Fg = fat globule. Bar = 1 μm. By courtesy of Dr. W. Buchheim, Kiel.

Figure 1 shows the air cell structure of an aerated, imitation dairy cream demonstrated by electron microscopy using the freeze fracture technique (3). The fat globules are adsorbed at the air-water interface, and protrude into the air cell to varying degrees. The driving force for this process is partial destabilization of the fat globules, from which the protective protein membrane is partly re-moved, making the fat globules more hydrophobic and thus forcing them to be oriented towards the air-water interface. Destabilization involves both a desorption of protein from the fat globule surface and crystallisation of the fat phase, both of which take place during the ageing period of an ice cream mix before freezing. Both these processes are essential for the final volume, texture and stability of ice cream, and both are enhanced by monoglycerides and other surface-active lipids.

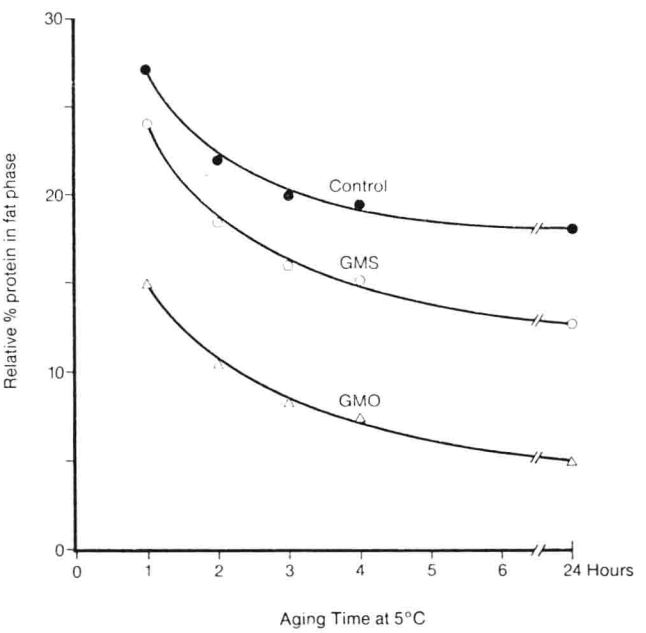

Figure 2. Changes in amount of protein absorbed to fat globules in an ice cream mix during the ageing period at 5°C. The amount of protein bound in the fat phase is calculated relative to the total protein content (4.4%) of the ice cream mix.

The desorption of protein from fat globules in ice cream mix during ageing is demonstrated in Figure 2.

Ice cream emulsions containing 10% fat with or without 0.2% emulsifiers were homogenized at 140 bar at 80°C, cooled to 5°C and aged at 5°C up to 24 hours. The emulsifiers used were distilled, saturated monoglycerides (DIMODAN PV, Grindsted Products, Denmark), referred to as GMS, and distilled, mono-unsaturated monoglycerides, iodine value 55 (DIMODAN OT, Grindsted Products, Denmark) referred to as GMO. Samples of each emulsion were taken at one hour intervals and centrifuged at low speed in order to separate the fat phase from the serum phase without subjecting the fat globules to coalescence. The protein content was then determined in the serum phase using the Kjeldahl method. The amount of protein bound to the fat phase was calculated as the difference between the total protein content of the whole emulsion and the amount of protein in the serum. When the mix was cooled to 5°C, desorption of interfacial protein took place. The addition of emulsifiers enhances the desorption process to varying degrees.

After homogenization of the emulsions, the protein load on the fat globules is lower when emulsifiers are added to the fat phase than when no emulsifiers are present. The actual protein load appears to decrease strongly at the initial stage of ageing at 5°C, especially with unsaturated monoglycerides (GMO) added. After four hours' ageing protein desorption levels off and only a slight decrease in protein load is found in the period between 4 hours and up to 24 hours' ageing time. The final protein load of the fat globules is determined by the type of emulsifier added. The emulsifiers which give a higher surface pressure (i.e. lower interfacial tension) than proteins at interfacial films will have a displacing effect on the proteins.

INTERFACIAL TENSION MEASUREMENTS

Oil/water systems containing milk proteins and emulsifiers were studied using the Krüss Tensiometer Model K10. The temperature of the o/w system was controlled by a thermostat which increased or decreased the temperature at a given rate. The interfacial tension was measured by the Wilhelmy plate method.

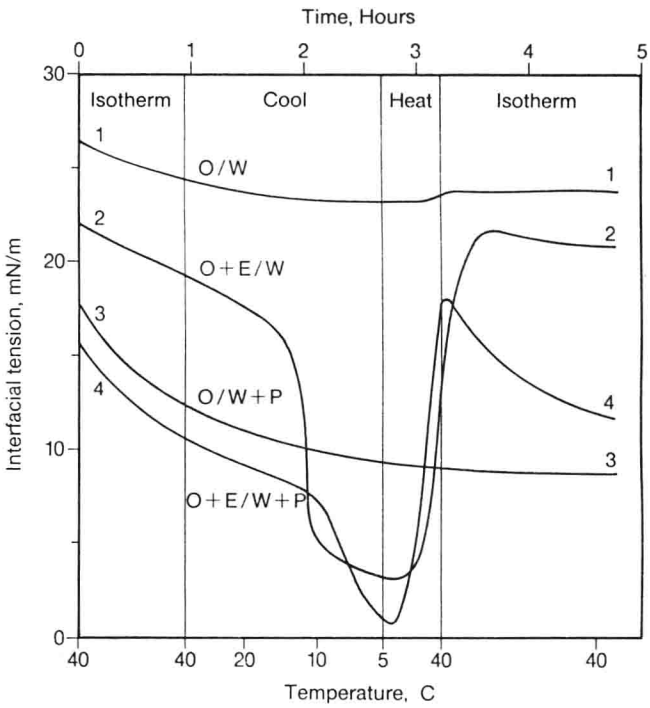

Figure 3. Changes in interfacial tension of oil:water interface with and without emulsifiers or proteins measured as a function of temperature. O = oil phase (sunflower oil), W = distilled water, E = 0.1% emulsifier (GMS or GMO) based on the oil phase, P = 0.01% milk protein based on the water phase.

Figure 3 shows the interfacial tension of various sunflower oil:water systems as a function of temperature. The temperature was first kept at 40°C for one hour, followed by cooling to 5°C at a rate of 0.3°C/min.

When the temperature of the oil:water system had decreased to 5°C, heat was applied via the thermostat. The temperature increased again to 40°C, where it was kept for about 1½ hours. The results show that the pure system of oil:water only drecreases slightly in interfacial tension when the temperature is decreased from 40 to 5°C. With 0.1% GMS added to the oil phase a considerable decrease in interfacial tension is observed when the temperature is below 15°C. At 5°C the interfacial tension is 3-4 mN/m. When re-heated to 40°C, the interfacial tension increases to the initial value of 21 mN/m. With 0.01% milk proteins in the water phase the interfacial tension reaches an equilibrium at 9 mN/m, and is not affected by changes in temperature. A combination of 0.1% GMS in the oil phase and 0.01% protein in the water phase shows that the interfacial tension decreases when the temperature is below 10°C to a value of 1 mN/m at 5°C. After re-heating the interfacial tension increases to a higher value than the initial value of 15 mN/m, which is achieved again after half an hour's equilibration time. The decay in interfacial tension at 40°C is due to the slow re-adsorption of protein.

This experiment shows that GMS becomes much more active as a surfactant when the temperature is lowered below 15°C, and due to this increased surface activity GMS can displace proteins from the oil:water interface. This displacement will take place when the interfacial tension (curve 2) of the emulsifier film intercepts with the interfacial tension (curve 3) of the protein film, which takes place at a temperature of about 12°C in the experiments shown in Figure 3. Recent experiments have shown that GMO performs similarly to GMS at low temperatures.

DISCUSSION AND CONCLUSION

The relationship between surface tension and temperature in emulsifiers was observed two decades ago by Lutton et al. (10). They explained that this relationship is due to a transition from a liquid-expanded type of mono-layer existing at high temperature (e.g. above 40°C) to a solid-condensed monolayers existing at a lower temperature (e.g. under 20°C). In solid condensed monolayers the molecular packing of the emulsifier molecules is much denser than in liquid expanded monolayers, and these differences result in lower or higher surface tension respectively.

Saturated monoglycerides form liquid expanded monolayers at 40°C, but on cooling to below 20°C a transition to solid hydrocarbon chains takes place, resulting in denser paking of the molecules and a decrease in interfacial tension.

Oil:water systems containing emulsifiers and proteins exhibit lower interfacial tension than systems containing only emulsifiers or protein which are added separately. This means that the interfacial film consists of both emulsifiers and protein units (see Figure 3). On cooling, the interfacial tension decreases in the same way as that of the system containing emulsifiers and no protein. This indicates that the emulsifiers increasingly dominate the interfacial film at low temperature, although some protein may still be present.

If a similar decrease in interfacial tension takes place in an ice cream mix during ageing at 5°C, this decrease will accelerate the desorption of protein from the fat globule surface. This mechanism may explain how monoglycerides promote protein desorption in ice cream mixes and other whippable emulsions.

When measuring the protein desorption from fat globules in ice cream mix aged at 5°C, GMO displayed a stronger effect than GMS, which results in a different texture and melting resistance of the final ice cream (3). The interfacial tension measurements at low temperature shows an increasing adsorption of monoglycerides at the oil-water interface. When the concentration of GMS molecules is increased it results in the formation of solid condensed mono-layers. In case of GMO a formation of a liquid-crystalline mesomorphic phase with cubic structure will take place, and this results in absorption of water into the surface of the fat globules. This mechanism has been demonstrated to take place in other whippable emulsions (11) and may account for the different behaviour of GMS and GMO in ice cream emulsions.

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PHASE SCIENCE OF EMULSIFIERS: SIGNIFICANCE AND RECENT DEVELOPMENTS IN METHODOLOGY

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The structure of food products has many qualitatively different dimensions—molecular, conformational, phase and colloidal. Arranging these various kinds of structural information in a hierarchy of relative complexity provides a useful perspective. The phase science of food emulsifiers is directly relevant to the phase structural level, and hence to the thermodynamics of the system. It is also true, but less obvious, that phase behavior influences colloidal structure.

Determining the phase behavior of emulsifiers can be difficult, but both qualitative isothermal swelling methods and the recently developed quantitative analog are readily applicable to food emulsifiers. Exploratory data illustrating the potential of these methods are presented.

The phase science of food emulsifiers is widely recognized as an important dimension of their physical science (1), and extensive phase studies of these compounds using classical methods have been reported.

In the first part of this paper the nature of the information provided by phase information on food emulsifiers, and the relevance of phase science to food technology, will be reviewed. In the second part, exploratory data will be presented which illustrate both the limitations of classical methods and the remarkable potential of swelling methods for producing reliable phase information.

RELEVANCE OF PHASE INFORMATION TO FOOD EMULSIFIER SCIENCE

To define the physical science of any system one must provide structural, thermodynamic, and kinetic information. Let us consider first "structural information".

The word "structure" is an ambiguous term. Nuclear physicists deal with "atomic structure" and every chemist is familiar with "molecular structure". Organic and polymer chemists deal with "conformational structure," phase chemists with "phase structure", and colloid chemists with "colloidal structure". Biological systems display exceedingly elaborate structures.

In order to perceive the relationships among these different dimensions of "structure", it is useful to arrange them in a heirarchy of relative complexity. Such a heirarchy is shown in Fig. 1.

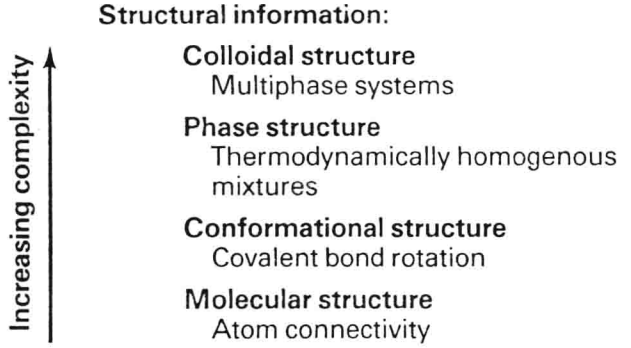

Figure 1. Structural information hierarchy

The simplest kind of chemical structural information is "molecular structure", which is fully defined by stating atom connectivity (which atom is connected to which). Stating

molecular structure provides by implication an immense amount of information about a pure substance, but does **not** constitute a full definition of structure - even of a single isolated molecule. This is because practically all molecules display facile isomerism due to rotation about covalent bonds (2). To define the shape of a molecule thus requires conformational structural information. Since more parameters must be stated to define conformational than molecular structure, the former is clearly more complex information than the latter.

These two lower levels of structure suffice to define an isolated molecule, but most chemical investigations involve samples which contain astronomically large numbers of molecules. Such a sample which is thermodynamically homogeneous is termed a "phase" (3).

Phases have characteristic structures. Phase structure may be very simple, as in gases and single crystals. It may be extremely complex, poorly defined, and impossible to describe using a simple drawing, as in liquids (4). Both crystal-like order and liquid-like disorder may exist in the same phase, in which case one has a "liquid crystal" phase (5).

Phase structure describes how aggregates of large numbers of molecules are arranged in space. Within each phase, molecules having a particular molecular and conformational structure, or distribution of structures, exist. Phase structure is thus more complex than is conformational structure.

A sample may be thermodynamically inhomogeneous, in which case it contains two or more phases. These are coexisting phases if they are in direct contact and in a state of dynamic equilibrium (3). With expenditure of sufficient energy in a proper manner, these various phases may be dispersed within one another in various ways. This level of structure is conveniently termed "colloidal structure". Broadly speaking, colloidal structures fall into one of two classes: sols, which contain discrete particles separated by a continuous matrix, and gels, which contain a network of one phase within a matrix of another (6,7).

In food systems one encounters structural complexity at least to the colloidal level. Simple real systems such as oil/water emulsions in salad dressings, stabilized foams in whipped cream (8), or concentrated dispersions of ice crystals in a mixture of liquid phases in ice cream (9), are reasonably well described using colloidal structure information. In other food systems still higher structural levels must be considered.

Structure is important because it often defines utility. In areas such as pharmaceuticals or molecular biology, molecular structure provides sufficient information to define intrinsic biological activity (10). Indeed modern biology has become synonymous with molecular interpretations of biological phenomena, because a direct correlation between molecular structure and these phenomena often exists.

In the foods area the nutritional value and other properties of foodstuffs **do** correlate with molecular structure. However, for many food properties molecular structure **per se** is inconsequential - except insofar as it anticipates other properties. Two properties of particular interest (with respect to the textural and aesthetic properties of foods (11)) are rheological and optical properties. The correlation between molecular structure and these properties is indirect and empirical. Such empirical relationships between molecular structure and those properties which determine utility apply to many consumer product technologies.

Structural information, in this context, is important mainly as a device for understanding and manipulating utility. Those elements of basic science which underlie and determine structure, and therefore properties, are of particular interest to the food technologist.

ROLE OF PHASE SCIENCE

The information which underlies phase and colloidal structure is thermodynamics. Thermodynamics is the cornerstone of physical science, because it is independent of rates, path, and mechanism. For the same reasons thermodynamics is by itself incapable of fully defining the physical science of most systems, which do not instantaneously reach equilibrium. As a result, kinetic and other kinds of information are also important.

Further, when a system possesses colloidal structure the rate of change of this structure may be slow. The existence of colloidal structure signifies the existence of an excess energy, commonly termed "surface energy". This kind of instability is diminished by the collapse of colloidal structure, so as to produce coexisting phases having minimal excess surface energy. (The excess surface energy can **never** be zero for coexisting phases, but it may be small in comparison with thermal or mechanical energy fluxes.) It is entirely possible that colloidal structure may never completely collapse.

It follows that there are kinetic aspects both to the attainment of equilibrium at the phase structural level, and to changes in colloidal structure. The two phenomena must be treated separately, because often equilibrium is quickly attained with respect to phase structure while colloidal structure collapses at a much slower rate (12).

For food systems, that branch of thermodynamics which is particularly relevant is phase science. Phase diagrams define, for systems in equilibrium, the range of system variables (temperature, pressure, and composition) over which smooth and continuous changes in phase structure and properties occur. They also define the coordinates of these variables at which discontinuities occur; the loci of these discontinuities are the phase boundaries. Thus phase information is essentially thermodynamic in nature, and is the most elementary form of thermodynamic information.

CORRELATIONS BETWEEN PHASE EQUILIBRIA AND COLLOIDAL PHENOMENA

Considerable information exists as to just how phase information is relevant to foods in the works of Friberg and Larsson.

Friberg has pioneered investigations of the correlations between phase equilibria and colloid stability. He has documented the fact when small amounts of the lamellar liquid crystal phase coexist with two liquid phases, emulsion stability is dramatically enhanced (13). Further, he has shown that when a foam is created from a mixture of a liquid and a coexisting lamellar phase, it is remarkably stable (14). Thus, it is actually possible to anticipate - by inspection of a phase diagram - the precise compositions which lead either to stability or to instability in foam and emulsion structure. This noteworthy application of phase information had not earlier been recognized.

Larsson has shown that the monoglyceride and polar lipid components of wheat flour lipids play an important role in the stabilization of foam structure during the baking of bread (15). Both gluten and flour lipids contribute to foam stability in this instance. As regards lipids, the formation of a lamellar liquid crystalline phase by compounds such as sugar diglycerides has been shown to contribute to foam stability. Conversely, lipid mixtures which form the hexagonal liquid crystalline phase within bread are comparatively ineffective in stabilizing the foam structure of bread.

The basis for all these phenomena lies in the fact that the lamellar phase - but not the hexagonal or cubic phases - is surface active. This phase spontaneously collects and spreads at interfaces (16). As a result interfacial tensions are lowered, and the drainage of liquid through foam membranes and the Plateau borders (13) at the intersections of these membranes is retarded.

The water-in-oil (L2) microemulsion (13) phases are oily and do not form stable emulsions unless the lamellar phase is present. They also diminish foam stability, possibly via Marangoni instability induced by their presence within interfaces (17).

FLAWS IN EXISTING PHASE INFORMATION

It is evident from the above that phase information on emulsifier-water systems is relevant to food technology. Important early contributions to the phase science of aqueous monoglyceride systems were made by Lutton (18), but it has been discovered that flaws exist in these data. To obtain a correct historical perspective it is worthwhile examining the Lutton diagram of a representative monoglyceride-water system, and the method by which it was determined.

It is evident from the monoolein-water diagram (Fig. 2) that this compound is poorly soluble in water and that water is soluble in monoolein to about 25%, depending on temperature. Ice and dry monoglyceride crystal phases, plus hexagonal, cubic, and lamellar liquid crystal phases, exist. Crystal hydrates apparently do not exist. No Krafft discontinuity (12) is seen over the temperature range of this investigation. The hexagonal phase, designated originally as the "middle" or oil-core phase, has since been found to possess the "inverted" or watercore structure (19).

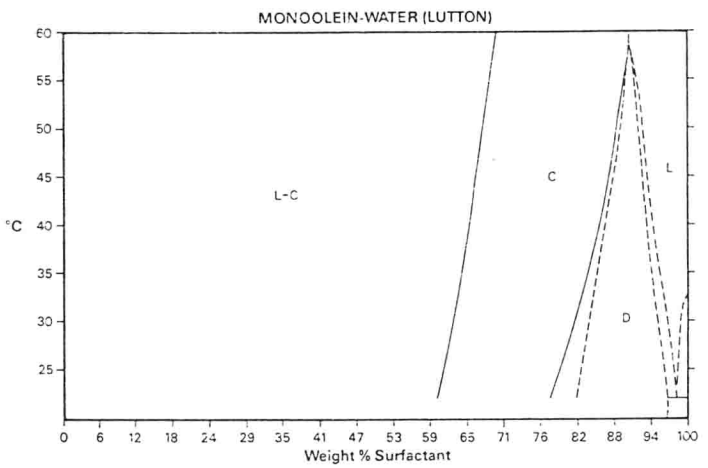

Figure 2. Monoolein-water diagram (Lutton)

This diagram was determined using the phase tube method, which is based on the isoplethal phase studies principle (20). (Isoplethal phase studies are performed by varying temperature at specific compositions and determining the temperatures at which discontinuities occur in the number of phases.) For this study numerous samples of known composition were prepared, sealed, mixed by centrifugation through an orifice, and heated and/or cooled while being observed between crossed polars. Phase structures were identified by observation of properties and of textures in the polarizing microscope (21), or by powder x-ray studies.

These studies are laborious and require large samples; further, the results are in some respects uncertain. For example several phase boundaries are dotted, because while they are presumed (on the basis of the Phase Rule) to exist, data which define their precise location do not exist. Indeed, in most surfactant-water phase diagrams (5) those boundaries which define the limits of liquid crystalline phase regions are ill-defined.

Continuing, the manner in which the lamellar liquid crystalline phase decomposes on heating is also uncertain. It is not even clear whether this phase decomposes congruently (to a single phase of the same composition) or incongruently (to two phases of different compositions) (3). Finally, the coexistence relationships of the hexagonal phase with other phases (not shown in Fig. 2) are unclear.

Questions such as these constitute elements of the basic phase behavior of this system which are extremely difficult to define using isoplethal phase study methods, but they are not insignificant. These uncertainties signify that the thermodynamics of heterogeneous equilibria in this system have not been fully established - even as to their qualitative aspects.

Exploratory Monoolein-water Diagram

This same system was recently

reinvestigated during exploratory studies of a wide range of surfactant systems using the new DIT (Diffusive Interfacial Transport) method (22) (Fig. 3). Briefly, the DIT experiment

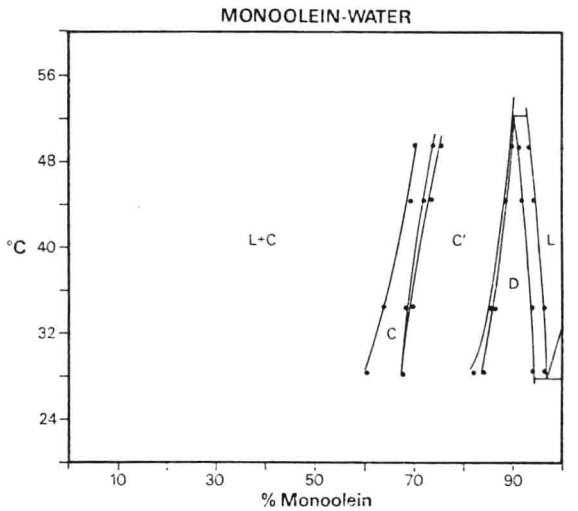

Figure 3. Monoolein-water diagram (preliminary DIT data).

is executed by creating an interface between the compound and water within a long, thin, capillary. After a few hours the swelling of the compound by water (principally via diffusive transport) creates a sequence of bands within the capillary. These bands correspond to the phase sequence at the ambient temperature, and composition discontinuities at the interfaces between the bands correspond to the miscibility gaps between the phases. Qualitative identification of the phase structure within each band, and quantitative determination of the compositions at interfaces, provides phase information.

In this monoolein study the full temperature range was not studied and the raw refractive index data have not been precisely correlated with compositions. However, the qualitative features of the diagram were precisely defined and compositions were estimated from the index-temperature profile of the dry compound, assuming a linear relationship between refractive index and composition. Compositions in the resulting diagram agree with Lutton's data to within ca. 3%, where it is possible to compare the data.

This DIT diagram also shows that the solubility of the compound in water is small, while water is relatively more soluble in the compound. However, two cubic phases were observed, separated by a small miscibility gap.

Only one cubic phase was recognized in the earlier study, which is hardly surprising in view of the narrow miscibility gap between them and the low level of scattering which exists when this phase is dispersed in another isotropic phase (23). (In fairness, it should be noted that the existence of the two cubic phases was recently recognized by Longley and MacIntosh (24) and by Larsson (25), using x-ray data. The convergence of the boundaries of the lamellar phase regions to a sharp cusp suggests that this phase decomposes **incongruently** at a peritectoid discontinuity (12). At the temperature of the cusp the phase disproportionates to a dilute cubic phase and a concentrated liquid phase.

This kind of behavior at the upper temperature limit of liquid crystal phases is not usually observed. Typically, liquid crystals decompose **congruently** to form a liquid phase (5).

Thus, it was possible during the DIT study, using milligrams of sample and about three days' work, to obtain phase information that was either accessible using other methods only with considerable effort (i. e. recognition of all the phases), or not at all (i. e. the compositions of coexisting phases and the nature of the discontinuities).

The $C_{10}E_4$-H2O System

Another instance in which the use of classical methods led to qualitative errors is the $C_{10}E_4$-H2O system. This system had been exhaustively studied by Lang (26), but we find nevertheless that the published diagram (Fig. 4) is not entirely correct. The phase behavior of this surfactant is unusually complex, due to interaction of the liquid crystal

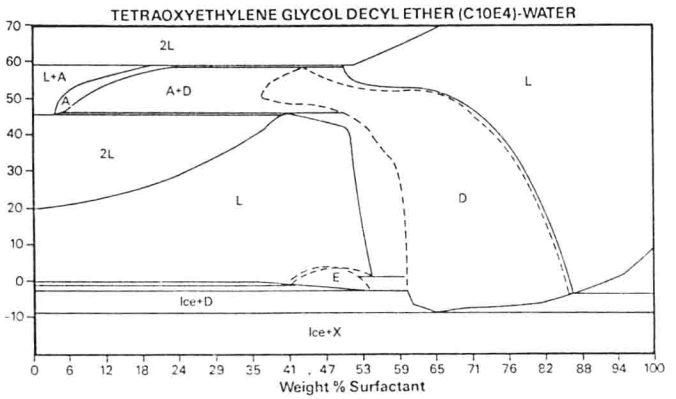

Figure 4. The $C_{10}E_4$-water system (Lang and Morgan)

region with the (cloud point) miscibility gap. This produces a corridor which cuts through the gap and creates a new (L_3 or anomalous) phase.

If one scans isotherms in the Lang diagram below 46°C, the phase sequence LLDL is found (using L for liquid and D for the lamellar liquid crystal). Between 46.00 and 46.14°C the sequence LLLDL is observed, and between 46.14 and 58.66°C the sequence LLDL is again found. We find using the DIT method these expected phase sequences - except near the lower part of the corridor. In Fig. 5 a sketch

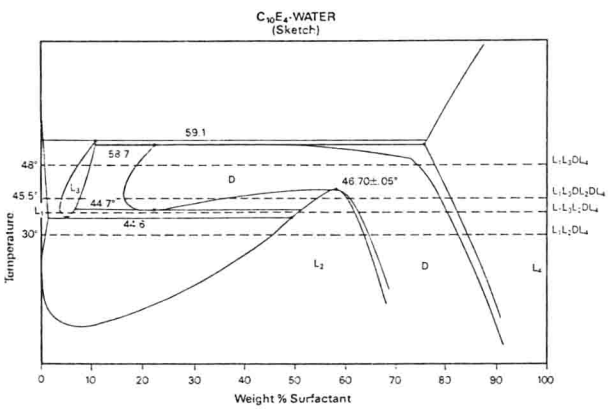

Figure 5. A sketch of the $C_{10}E_4$-water diagram. The temperature scale has been distorted so that the qualitative features suggested by DIT data are visible. The phase sequences along specific isopleths are noted to the right.

of a revised diagram is presented in which the temperature scale is severely distorted. In this way the qualitative features of the phase behavior are visible.

The most significant change is the insertion, above the LLLDL regions, of a **six-phase** LLDLDL region spanning a 2°C range. Nowhere in the published diagram do isotherms exist across which six phases are encountered. This situation results from the intrusion, from below, of the L2 region into the lamellar liquid crystal region. The modification required by the new data is elimination of the cusp at 46% and 46°C in the L2 phase. Instead, the boundary of the L2 phase is smooth and continuous, and the phase terminates at an upper azeotropic point. Such behavior has not previously been observed in surfactant phase studies - and is altogether remarkable. It signifies that **a liquid crystal is formed by heating a micellar solution.** (Actually, this sequence of events does occur, rarely and over narrow composition ranges, when the liquid crystal solubility boundary displays a bulge towards the water axis (5,23).)

SCOPE AND LIMITATIONS OF SWELLING METHODS

These recent investigations of monoolein and $C_{10}E_4$, as well as other information (27), illustrate the fact that the status of phase diagrams of even the most thoroughly studied systems may be uncertain. They further illustrate the value of using swelling methods during phase studies. These methods will in time become widely used, and it is therefore worthwhile reviewing their scope and limitations. The advantages include:

Efficiency. In each experiment, the phase sequence along an entire isotherm is displayed within a few hours' time. Five minutes are required to quantitatively scan an interface using the DIT apparatus. The calibration of these data presently requires considerably more work, and calibration methods are still being refined.

Thoroughness. The chances of missing a phase are smaller using swelling methods than by any other, because composition is varied in a smooth and continuous manner. In order to insure detection of interfaces it is necessary to observe the